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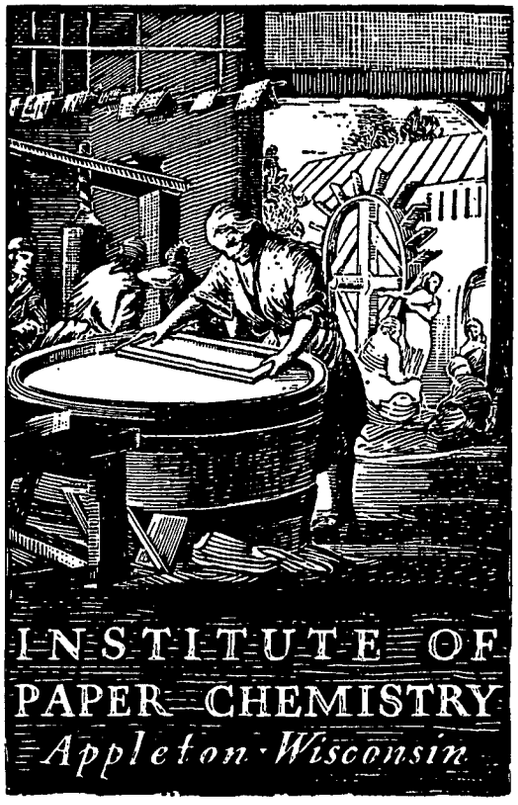

STUDY OF THE CARBOHYDRATE PEELING AND STOPPING REACTIONS UNDER THE CONDITIONS OF OXYGEN-ALKALI PULPING

Project 3265

Report Two
Final Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

September 3, 1976

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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A Progress Report

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SUMMARY

Dissolved oxygen solutions were prepared by spraying various solutions into a container pressurized with oxygen; this technique took only a few seconds. The solubility of oxygen in sodium bicarbonate is much less than that in sodium hydroxide of equal normality. The plots of dissolved oxygen versus pressure showed good agreement with Henry's Law. Analysis of these systems was obtained by use of a stainless steel trap pressurized with nitrogen and containing Winkler's reagent. It was found that such pressurized systems gave a rapid reaction of the dissolved oxygen with the reagent; in contrast in unpressurized systems most of the dissolved oxygen escaped and the resulting gas reacted very slowly with the reagent.

The use of a high performance liquid chromatograph has been explored with the aid of a universal detector (moving wire type). The Waters μ-Bondapak column, designed for the separation of carbohydrates, gave good separation of oligosaccharides (cellodextrins) up to DP = 7. Sugar acids however were absorbed on this type of column and were eluted only with dilute phosphoric acid. The use of such a column in the "neutral" and "acid" forms to separate sugars from their acidic oxidation products is discussed.

Studies of the role of hydrogen peroxide and oxygen in various buffer systems with the glucosidic bond (methyl glucoside as a substrate) showed a strong adverse effect for sodium carbonate or bicarbonate in contrast to that for stronger alkali. It is postulated that glucosidic bonds are degraded during delignification reactions by the formation of a carbonate radical; the latter is formed by the interaction of hydroxyhydroperoxy radicals and carbonate or bicarbonate ions. This

carbonate radical can participate in further degradations, leading to losses in viscosity and lower pulp yields.

INTRODUCTION

The purpose of this project is to study the relative rates of peeling of glucosidic end groups in comparison to the stopping (oxidation) of these same end groups in a system composed of oxygen and alkali or buffer system of lower pH. Experimentally the problem is to prepare solutions of dissolved oxygen under pressure in various alkaline or buffer solutions, to analyze for the oxygen content of these solutions, to control the oxygen while these solutions are mixed with various carbohydrate solutions at different temperatures, and to analyze the resulting systems for extent of reaction of the carbohydrates, either by oxidation or by peeling.

In the work cited in Progress Report One for this project it was demonstrated that dissolved oxygen solutions could be prepared under pressure and that they could be controlled by nitrogen pressure when the supporting oxygen atmosphere was removed. The concentration of dissolved oxygen was determined by the use of oxygen probes which were calibrated for high concentrations not normally encountered in the field of water analysis.

In the present work the chemical analysis of pressurized systems containing high concentrations of dissolved oxygen has been shown to be more reliable than the use of oxygen probes, where diffusion through Teflon membranes and electrode response have been shown to be uncertain variables. Also a technique of spraying aqueous solutions into a pressurized atmosphere has given a very rapid mass transfer of oxygen in the aqueous phase, in contrast to techniques of stirring or bubbling oxygen through a tower or packed column.

The role of hydrogen peroxide as an intermediate in aqueous systems containing oxygen has also been studied, in an effort to provide some background to our flow-reactor systems.

The relative merits of gas chromatography and liquid chromatography are discussed, and experiments cited to show the relative merits of each in analyzing reaction systems for unreacted carbohydrates and oxidation products.

A moving wire detector was used in the liquid chromatography studies; this universal detector gives peaks equivalent to the carbon in the nonvolatile solute removed from a given column and eliminates the problem of solvents passing through the detector. Before this detector was obtained, extensive work was done in attempting to convert various sugars and sugar acids to UV-absorbing compounds, this work was stopped when the new detector was obtained.

DETERMINATION OF DISSOLVED OXYGEN IN A PRESSURIZED WINKLER TRAP

The concentration of dissolved oxygen, prepared in high concentrations under oxygen pressure, is determined by forcing a known volume of solution into a trap containing Winkler solution. The iodine liberated is titrated with thiosulfate.

The Winkler solution is more dilute than that used in normal water analysis, and the trap is maintained under nitrogen pressure to prevent the dissolved oxygen from escaping from the solution. It was found that dissolved oxygen reacts rapidly with the reagent, but gaseous oxygen reacts very slowly. Most of the latter will bubble through the trap without reacting.

The construction of the trap and its operation are described, also two valve panels, one for the trap and the other for connections to the flow reactor, and a pressure chamber for the preparation of dissolved oxygen.

INTRODUCTION

The reaction of Winkler's solution (1) with oxygen is a conversion of manganese hydroxide to a higher valence state. The alkaline reaction mixture, also containing sodium hydroxide and potassium iodide, is then acidified and the iodide reacts with the manganese, forming free iodine. The latter is titrated with thiosulfate. The stoichiometry of the reaction is such that one equivalent of thiosulfate equals 8 grams of oxygen, or one ml of 0.025 normal thiosulfate is equivalent to 0.200 mg oxygen.

The normal procedure for the Winkler test is the addition of a very small volume (2 ml) of alkali-iodide solution and then of manganese sulfate (2 ml) to a large volume (250-300 ml) of water containing a small amount (8-10 ppm) of dissolved

oxygen. In our work we add a relatively small amount of water (20.7 ml) containing a high concentration of dissolved oxygen to a slightly larger volume (40 ml) of manganese hydroxide suspended in alkali-iodide solution. The amount of alkali-iodide and manganese sulfate solution used, though diluted, is equivalent to 5 ml each of the original reagents. The diluted reagents allow for better mixing of the reagents with the smaller volume of sample in the trap.

The Winkler method is normally carried out in a bottle that is almost completely filled to prevent access of air. In our work we flush the trap with nitrogen to remove air; also the trap is pressurized with nitrogen to prevent escape of dissolved oxygen from our samples when the original oxygen atmosphere is removed*. The solution of dissolved oxygen is forced from a hydraulic syringe (part of the flow reactor) into the trap. The reaction of the solution with the reagent is very rapid. The pressure is then relieved, acid added, and the reaction mixture removed from the trap by nitrogen pressure for analysis.

The function of the nitrogen pressure in keeping the dissolved oxygen in solution was discussed in Report One for this project (2); there it was used to keep the dissolved oxygen in solution as it was pumped through the flow reactor.

*Allowing the pressurized solution of dissolved oxygen to run into the Winkler trap at atmospheric pressure gave only a small reaction. Most of the gas evolved at this low pressure bubbles rapidly through the trap and subsequent shaking of the trap, still containing a gas, gave a very slow reaction with the reagent. In summary the gas reacts very slowly with the Winkler solution, in contrast to the rapid reaction of dissolved oxygen.

EXPERIMENTAL

The trap, shown in Fig. 1, is made of stainless steel tubing, two inches ID[1] x 7 inches long, and with a wall thickness of 3/8 inch. The tubing is capped at each end with a circular piece of stainless steel, 2 1/2 inches in diameter and 1 1/4 inches thick. The bottom cap has a slight well to allow complete removal of liquid from the trap. The top has three holes tapped to 1/8-inch NPT[2]. The two caps are welded to the tubing.

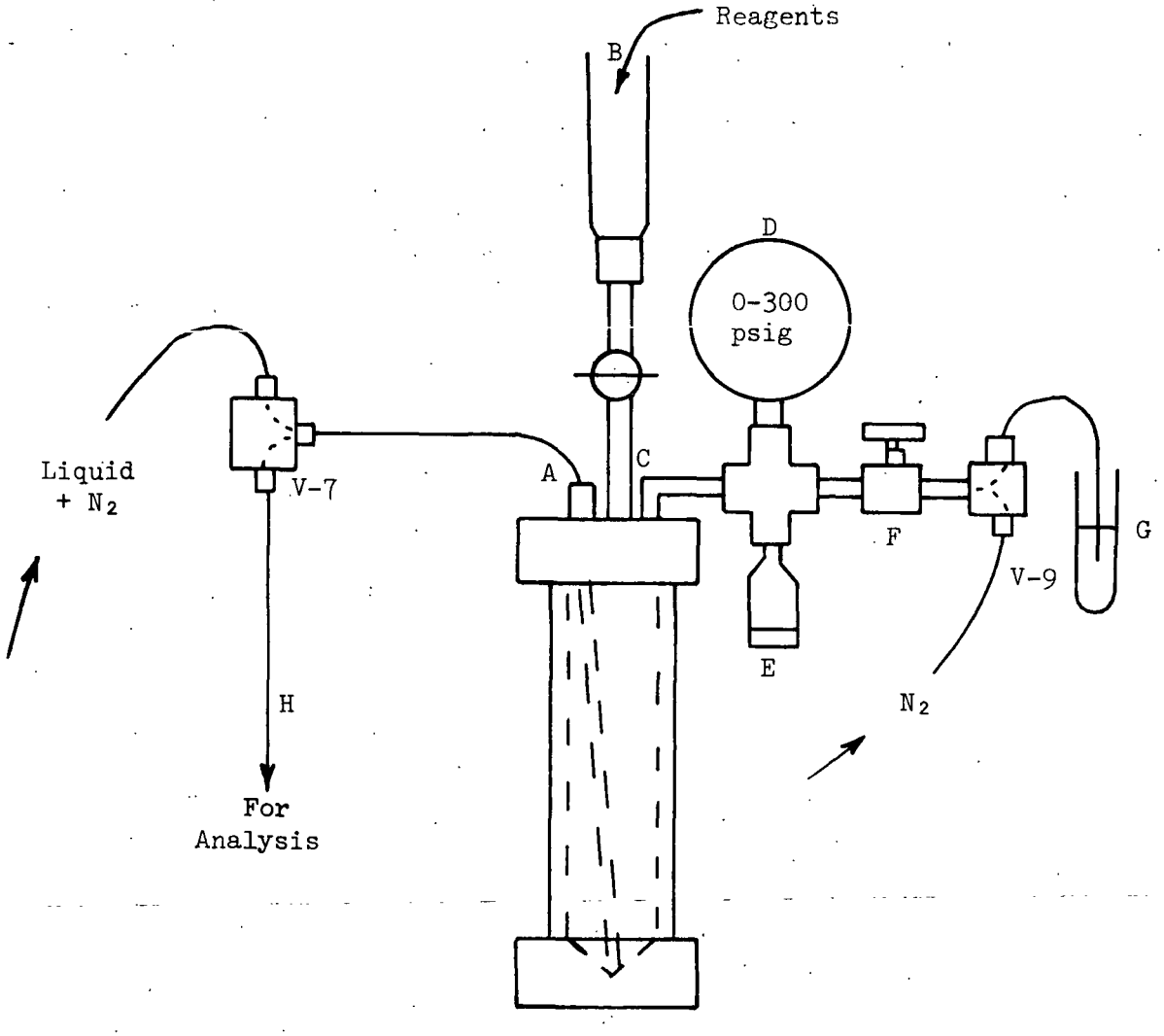


Figure 1. Pressurized Winkler Trap

[1] ID = inside diameter.
[2] NPT = normal pipe thread.

A is the inlet tube, bringing the liquid into the reagent within the trap. It is a length of 1/8 inch nickel tubing, 0.085 inch ID, inserted through a Swagelok male connector with 1/8 inch NPT fitting. The body of the connector is supplied with a 3/32 inch bore, and this was drilled out to a little over 1/8 inch to allow the nickel tubing to pass through. The tubing was pushed through the connector until it reached the bottom of the trap and was then secured with a ferrule and locking cap.

B is a funnel to introduce liquid reagent into the trap. It consists of a Whitey two-way ball valve mounted between two long hex nipples (1 inch x 1/8 inch NPT). The lower nipple is secured to the upper cap of the trap and the upper one is connected by a piece of rubber tubing to a glass funnel made of 14 mm tubing.

C is a male elbow, 1/8 inch NPT, connected via a cross (1/4 inch NPT) to a pressure gage D, a rupture disk assembly E and a needle valve F. F is connected to a three-way Whitey valve V-9, leading to a bubbler G, and to a nitrogen line. The action of valve V-9 is to connect F with either G or the nitrogen line, but G and the nitrogen line cannot be connected.

Finally the liquid sample, containing dissolved oxygen and nitrogen are led into A via ball valve V-7 (<u>forward flow</u>) (Fig. 2). When a <u>reverse flow</u> of nitrogen is used, introduced at valve V-9, the liquid is forced out of the trap through V-7 into line H, which leads to a collection flask for titration.

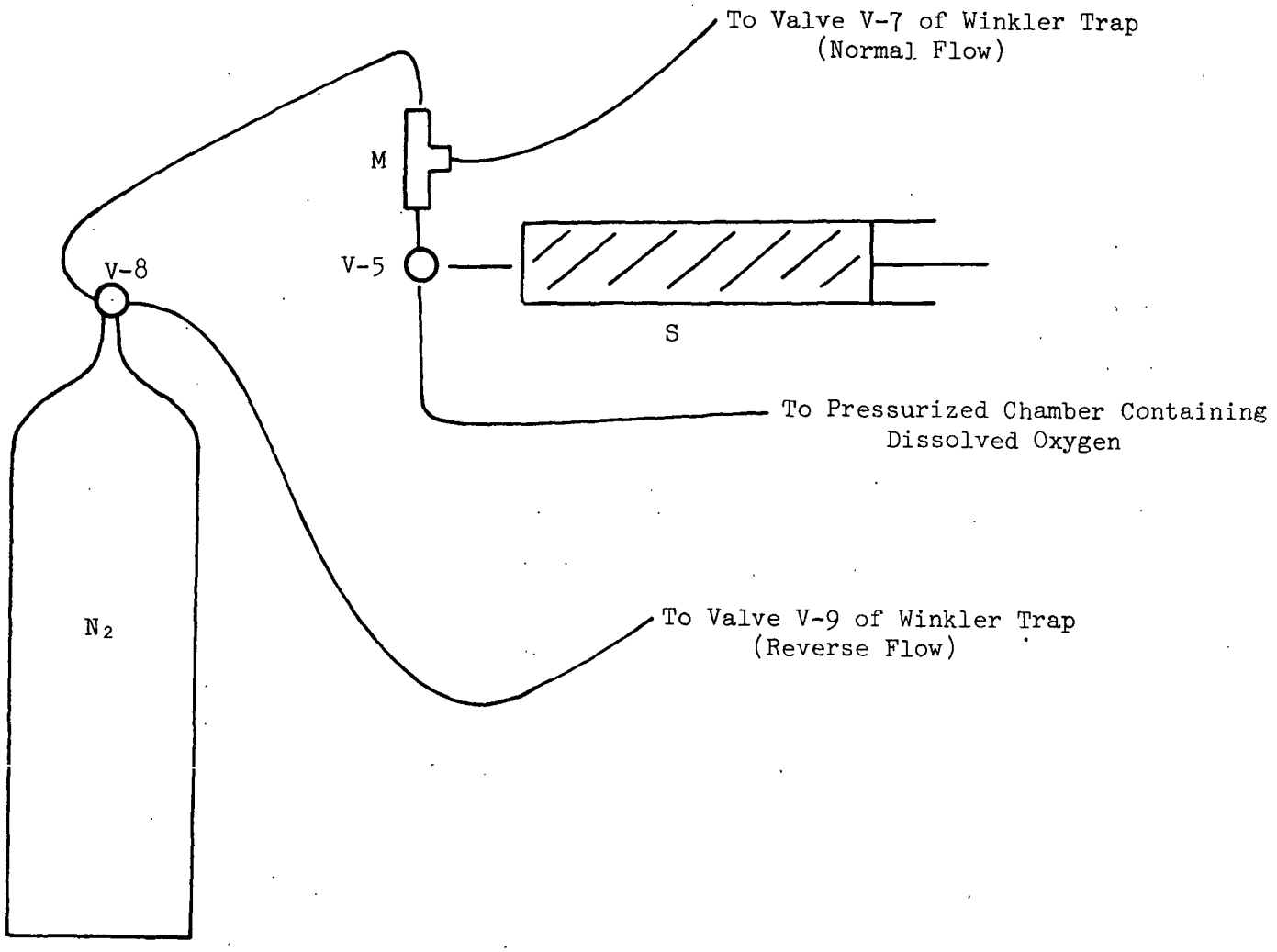


Figure 2. Connections of Syringe to Feed Lines

VALVE PANELS FOR FLOW REACTOR AND WINKLER TRAP

The number of valves controlling flow of liquids has become quite large, so two panels were made up, one holding five valves for the flow reactor and another holding three valves for the Winkler trap. The connections of these two panels to each other and to the oxygen pressure chamber are shown in Fig. 3. The details of the two panels are shown in Fig. 4-6. Each of the valves is a two-way mode, and in several cases two of them are connected directly by short leads to provide a three-way pattern of flow.

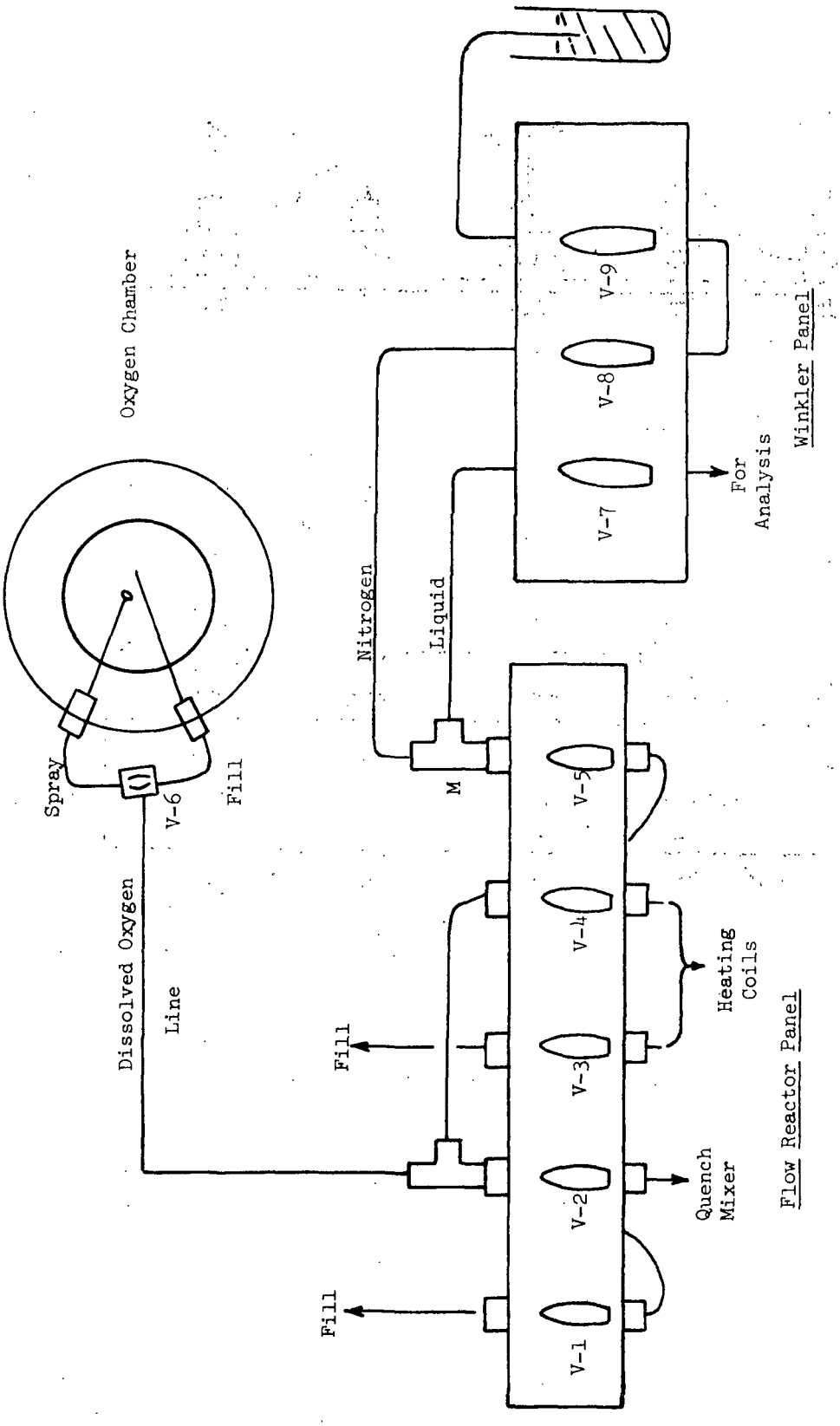


Figure 3. Connections of Valve Panels and Oxygen Chamber

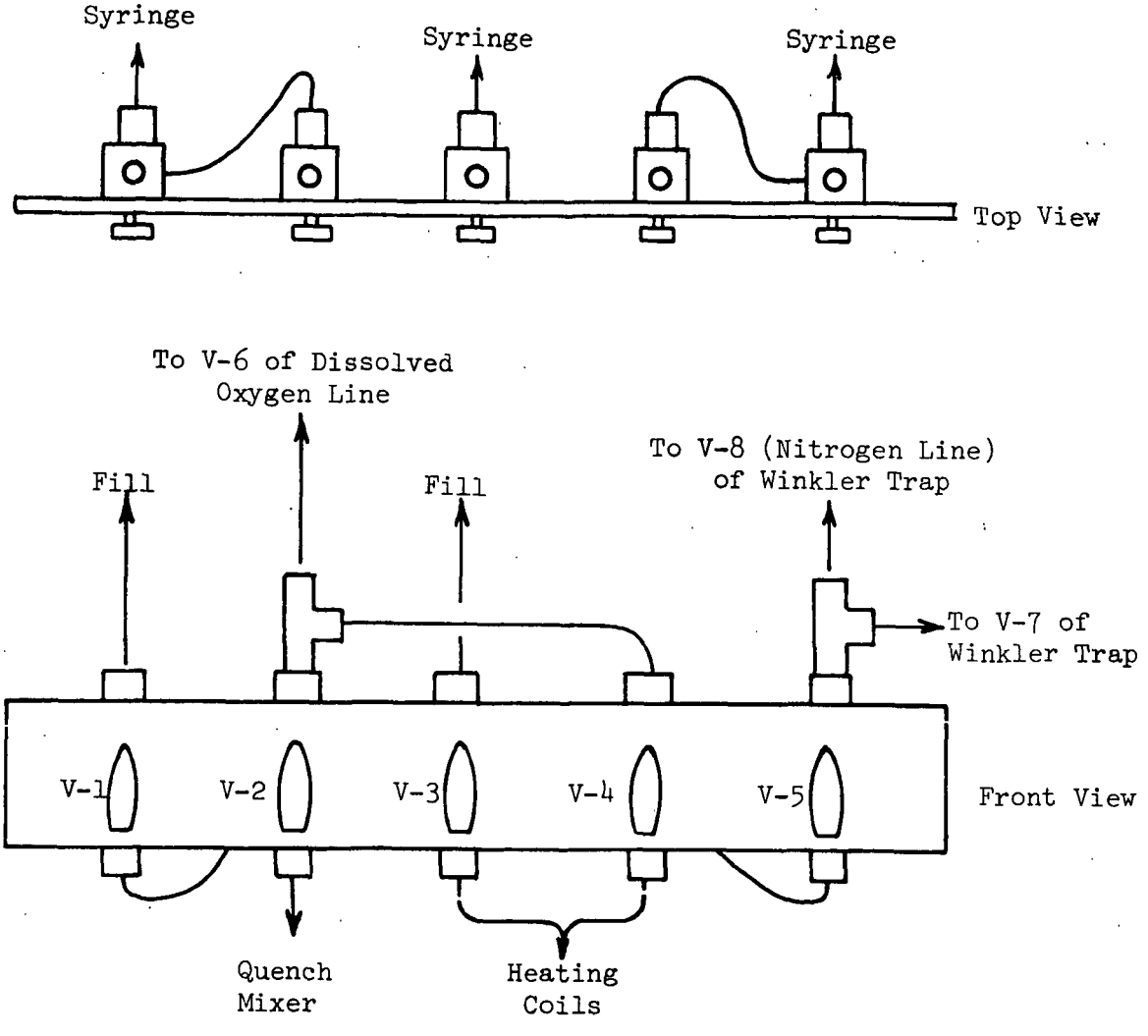


Figure 4. Valve Panel for Flow Reactor

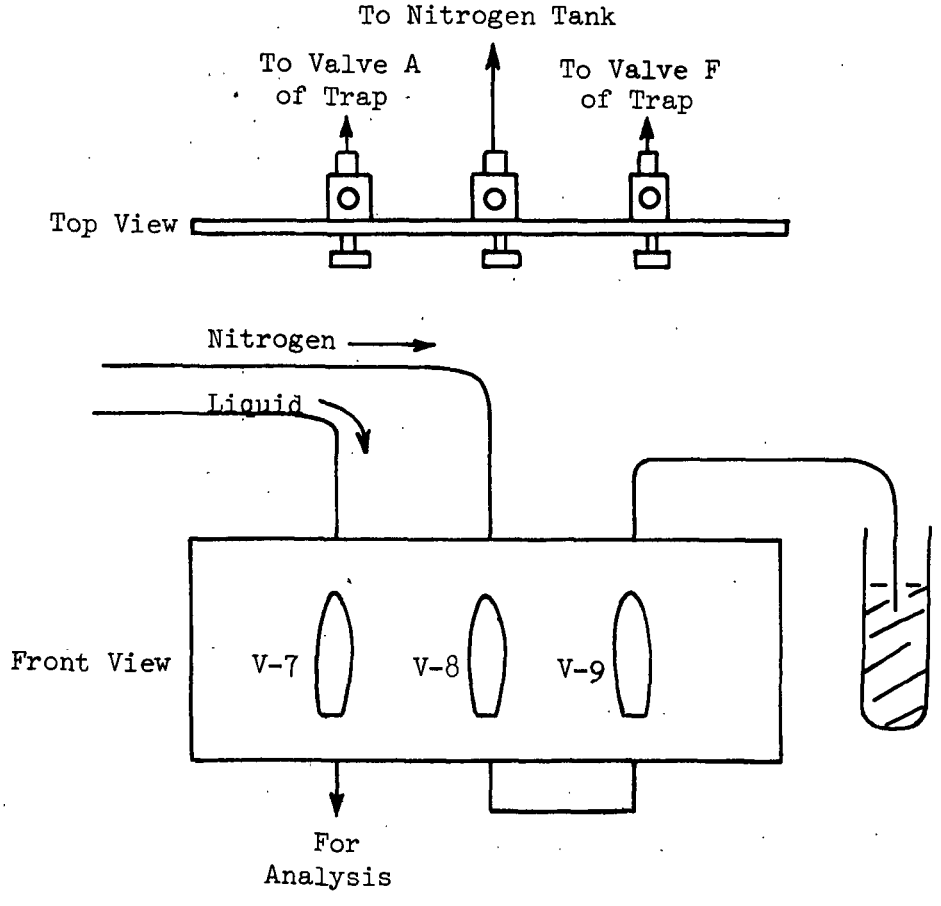


Figure 5. Valve Panel for Winkler Trap

The valve panel of the Winkler trap (Fig. 5 and 6) simplifies operations in that when all three valve handles are pointing up, the nitrogen flow through the trap is in a forward direction. When the handles are all down, there is reverse nitrogen flow which drives the reaction solution out of the trap (at V-7) for subsequent titration.

In all of these operations valve V-6 on the oxygen chamber must be operated in either a spray pattern (Fig. 3) or in a fill pattern to transfer solution into one of the mix syringes for either analysis in the Winkler trap or into a heating coil for subsequent reaction with a carbohydrate substrate. We thought of putting this valve on the reactor panel, but the dissolved oxygen line (see Fig. 4) is about 5 feet long, and replacing this with two pieces of tubing did not seem practical.

It is hoped that these panels will help the operator in various operations. With each modification of the reactor, it becomes more complicated, and the present arrangement of valves should hopefully counteract this in part.

WITHDRAWAL OF A SAMPLE OF DISSOLVED OXYGEN UNDER PRESSURE

A hydraulic syringe* from the flow reactor is connected by a three-way ball valve V-5 to a supply of dissolved oxygen in a pressurized chamber, and to a tee M, which leads to both the Winkler trap and to a nitrogen source (Fig. 2 and 3). The latter enters from valve V-8 which is connected to a nitrogen tank. Valve V-8 can thus introduce nitrogen into the Winkler trap at either end, at V-7 or at V-9 (forward flow or reverse flow).

*This syringe, made of stainless steel, is driven by a hydraulic ram at pressures up to 1,000 psig, so its movements are not affected by the much lower pressure of the chamber containing dissolved oxygen (150 psig maximum).

The sample of dissolved oxygen to be analyzed is 20.7 ml and is removed by adjustment of valve V-5 and retraction of syringe S. Valve V-5 is then turned and the syringe advanced to force the solution into tee M and to the trap.

METHOD OF ANALYSIS

The Winkler reagent consists of three solutions: (1) an alkali-iodide reagent consisting of 100 g NaOH and 30 g KI in one liter of water; (2) manganese sulfate solution containing 634 g $MnSO_4 \cdot H_2O$ in one liter of water; (3) dilute sulfuric acid of 7N concentration. The thiosulfate used in titration of the liberated iodine is of 0.025N cocentration.

The procedure has ten steps, which are outlined below, some more details are given later.

1. Add NaOH-KI solution (Solution 1) to trap, and flush with nitrogen for 5 minutes.

2. Add $MnSO_4$ solution (Solution 2) to trap and flush with nitrogen for 1 minute.

3. During this time pump liquid out of and in the oxygen chamber via valves V-4 and V-5 three times; then the syringe is finally filled. This is done at a flow control setting of 100, and about 30 seconds is allowed for each filling.

4. The Winkler trap is pressurized to 215 psig* by closing needle valve F, and allowing nitrogen to enter via V-8 (upward). Valve V-8 is then turned down, and V-7 and V-9 left in an upward position.

5. Valve V-5 is opened to connect the syringe with the trap, and the syringe advanced (flow control at 100) to push the liquid sample into the trap. A pressure rise to 230 psig can be noticed with this introduction of liquid.

*psig = pressure in pounds per square inch read on the gage; psia = pressure in actual pounds per square inch. Zero psig = 15 psia.

6. Valves V-5 is turned downward, needle valve F opened slightly and valve V-8 turned up to maintain a slight flow (at 200-215 psig with venting) of nitrogen through the trap. This is done for about 30 seconds.

7. Valve V-8 is turned down, and the pressure in the trap released.

8. Add sulfuric acid (Solution 3) to acidify the reaction mixture, then follow with a nitrogen flow as a stirring action to dissolve manganese hydroxides.

9. Remove the acidified solution by a reverse nitrogen flow.

10. Titrate the free iodine with thiosulfate.

Additional directions are given below for several of the above steps.

1. Initially the empty trap is filled with 25 ml of Solution 1 and the funnel rinsed with 10 ml water. This 35 ml of solution is treated with a stream of nitrogen (led in via A) for 5 minutes. Valves F and V-9 are open to the water trap G, so that the rate of bubbling can be qualitatively noted. Funnel D is closed at this stage.

2. The nitrogen flow is stopped at V-8, and 5 ml of Solution 2 added via funnel B. Nitrogen flow is then resumed for one minute to mix up the precipitate of manganese hydroxide.

8. The trap, now at atmospheric pressure, contains a mixture of oxidized manganese hydroxides. This solution is acidified by addition of 10 ml of Solution 3 through funnel B and 10 ml rinse water. To allow thorough mixing of the acid and to effect complete solution of all manganese hydroxides, a "lively" stream of nitrogen is passed through the trap at A.

9. The nitrogen flow is stopped, funnel B opened to relieve all pressure in the trap and the valve V-7 opened to line H. The line H is then placed in a 250 ml Erlenmeyer flask, B closed, and a slow pressure of nitrogen applied at V-9. This forces liquid out of the trap at A. A little wash water is added at B to remove the last traces of solution in the trap.

10. The acidified solution containing free iodine and KI is titrated with 0.025N thiosulfate, with Thyodene as an indicator.

ADDITIONAL COMMENTS ON THE METHOD

Vigorous stirring of the trap by a strong nitrogen flow does not seem to splash solution out of the trap into the pressure assembly; the water in trap H does not give a color with Thyodene.

Blank runs, without the addition of dissolved oxygen, gave titrations of about 1 ml of 0.025N thiosulfate, equivalent to about 0.200 mg oxygen. The 40 ml of solution in the trap (before acidification) could contain at best about 10 ppm oxygen, and this would amount to about 0.400 mg oxygen. So about half of the dissolved oxygen in the reagents has been removed. The main function of the nitrogen should be to remove this oxygen, since the gaseous oxygen in the atmosphere above the trap would react slowly.

Originally the Winkler trap was maintained under nitrogen pressure while the liquid sample was driven from the syringe into the trap. At this time a small flow of nitrogen was passed from valve V-8 through the above valve V-5 (Fig. 4) through V-7 into the trap and out through valve V-9. This constant flow was effected by opening the needle valve F (see Fig. 6) slightly and increasing the flow of nitrogen at V-8 to maintain the desired pressure (about 215 psig). This flow was done to insure that no liquid from the syringe would move into the nitrogen line rather than through the liquid line. Now this has been changed, and valve V-8 is closed (downward); after pressure is obtained in the trap, this valve is opened to create a nitrogen flow only after all syringe movement has stopped. Erratic results were obtained in some analyses by the first method, and it was felt that the nitrogen flow may have "chased" oxygen gas out of the liquid sample. Now the

trap is kept closed during the introduction of the liquid sample; a pressure rise from 215 to 230 psig can be seen.

LIMITATIONS OF OXYGEN PROBES

Originally in this project much work was done with probes, which measured the dissolved oxygen concentration electrically (3). As the project moved along, with the know-how obtained from these probes, we developed a chemical method, a modification of the Winkler analysis, for concentrations of dissolved oxygen. We have found this to be more reliable than the probes, especially at higher pressures. The action of the probes depends on the diffusion of gas through a Teflon membrane and often these membranes do not function too well. Thus at times the probe will not read above 200 ppm, and in other cases it will read up to 500 ppm, but when the pressure is released, the probe will still give a high reading, until the membrane is changed. Apparently the gas does not move in and out through the membrane too readily from liquids at higher pressures. We have found a rapid response (about 3 minutes) for the probes in an oxygen gas at various pressures, but when the probe is left in a liquid for some time, the original calibration is lost.

The probe does have the advantage of a rapid reading, when it does work well. In contrast the Winkler method takes about 15 minutes, most of this being operator time. Research on improving the reliability of the membrane action of the probe would be desirable, but it is not appropriate at this stage of our project.

Determination of Dissolved Oxygen at Higher Temperatures

The present Winkler trap is attached to the flow reactor and is designed to analyze for dissolved oxygen at room temperature. The flow reactor has heating

coils to raise the temperature of the dissolved oxygen solutions after they have been prepared and analyzed.

We are interested in the possibility of determining oxygen concentrations of solutions above room temperature, i.e., at pulping temperatures. This would involve two modifications. (1) Construction of a mobile unit, so that it could be wheeled to a digester to take a sample. Such a unit would contain a hydraulic pump, a single syringe of known volume connected to a hydraulic ram, forward and reverse controls, a Winkler trap, and valves for pressurizing the trap and connecting it to the syringe and the digester. (2) A system of cooling the hot liquid before analysis. A syringe of heavy construction would have enough mass to reduce the temperature rapidly. Mixing the hot liquid with an equal volume of cold water in the syringe might be effective also.

Such an assembly would allow us to find the steady state concentration of dissolved oxygen present during a pulping run. At present only the oxygen pressure above the system is measured, and very little is known of the mass transfer of this gas into solutions at different temperatures. With our spray technique we might be able to evaluate the effect of electrolytes as well as temperature on the surface characteristics of aqueous films and subsequent mass transfer of gases.

A SPRAY TECHNIQUE FOR THE RAPID MASS TRANSFER OF OXYGEN INTO AN AQUEOUS PHASE

Dissolved oxygen can be prepared rapidly by spraying water (or an aqueous electrolyte solution) into a bottle maintained under high oxygen pressure. The amount of oxygen dissolved is about 80% of saturation. The concentration is determined by subsequent analysis in a pressurized trap.

THE MASS TRANSFER EFFECT IN PREPARING DISSOLVED OXYGEN

The preparation of dissolved oxygen in aqueous systems involves the mixing of a gas and a liquid phase. Two major methods cited in treatises on mass transfer for dissolving gases are (a) creation of fine gas bubbles by use of a stirrer to break up the gas as it emerges from a sparger (4) and (b) the countercurrent movement of liquid and gas through a packed column (5). We have tried both methods and found them to be relatively ineffective in our pressure systems. The creation of bubbles involves a pressure differential for the gas, and such a differential is difficult to maintain at high pressures unless a constant venting of gas is used. So we have tried a third approach, that of maintaining the gas at a high and constant pressure, and spraying the liquid into this gas in the form of a fine mist. The mist, formed in a few seconds, drains into a bottle, and can be removed and sprayed repeatedly. The movement of the liquid is done with a syringe, driven by a hydraulic ram, and the fast flow of liquid through a fine orifice onto a splash plate creates the mist. The solution of gas is quite rapid under these conditions.

Sherwood, et al. speak of internal circulation within the liquid drops being caused by "gas-liquid shear forces" (6). Thus the absorption of carbon dioxide into 5-mm diameter drops of water falling freely was 50 to 70 times greater

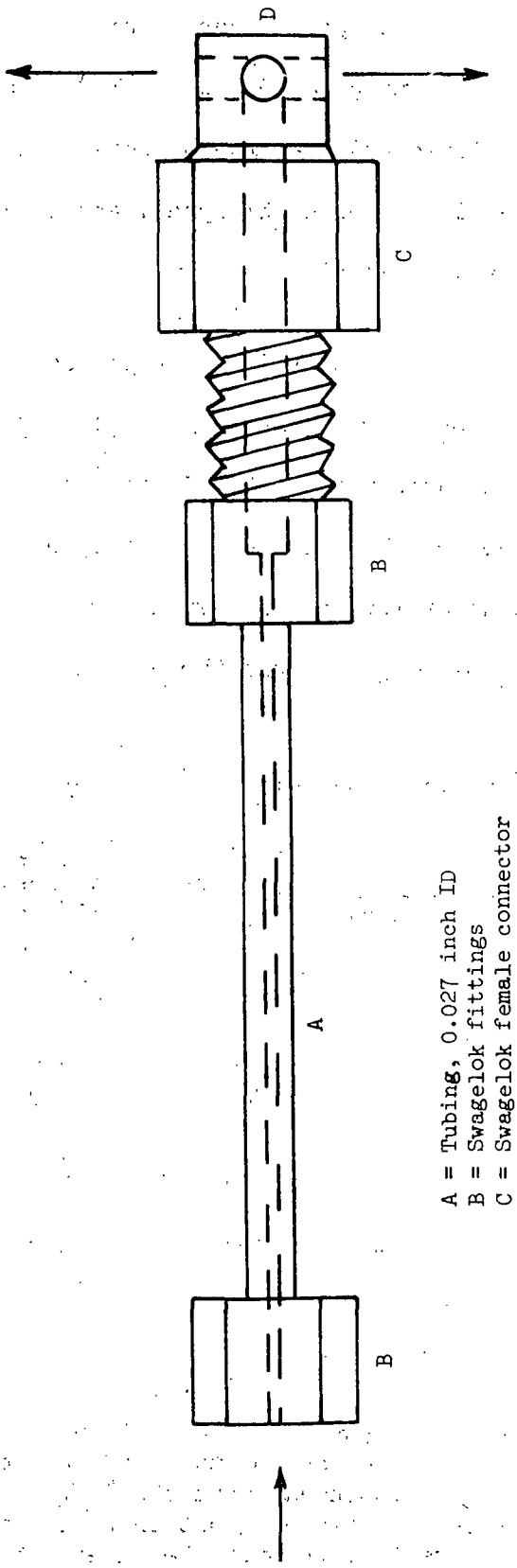
than that predicted for "transient molecular diffusion in a sphere." In our experiments the drops produced are very fine, probably much less than a mm in diameter. On the other hand we do not have a countercurrent flow, but just the quick fall of these drops for only a short distance, about 10 cm. For a short exposure time of drops into a gas, Sherwood (5) found that water was only 22% saturated with carbon dioxide for a fall of 52 cm through the gas. Since these drops were quite large, about 5.5 mm, the surface exposed was much less than ours. So we are happy to be able to obtain a value of about 80% saturation. The time of exposure is about 8 to 11 seconds.

The repeated spraying of the same liquid has been suggested, and we have tried that by removing our liquid from the bottle via a delivery line and pushing it back through the spray nozzle. However, the first spray seems to be the most effective. One problem we may encounter is the possible loss of oxygen when a suction effect is created by the retraction of the syringe.

It is interesting to note that this spray technique for transfer of oxygen to an aqueous solution was reported by Grangaard (7) for the oxidation of waste lignin products with oxygen and alkali at 160-170°C; the patent mentions a "spray nozzle or perforated cone" in the digester employed. Later Clayton and coworkers (8) carried out pulping studies with alkali and oxygen and noted that the "most efficient and most uniform pulping was obtained" when the pulping liquor was circulated through a sprayhead into an oxygen atmosphere.

CONSTRUCTION OF THE SPRAY NOZZLE

The spray nozzle shown in Fig. 7, is a 2-inch length of stainless steel tubing of small inside diameter, ending in a hollow plug with side ports. The liquid is forced through the narrow tubing at high velocity (about 100 km/hr) and



A = Tubing, 0.027 inch ID
B = Swagelok fittings
C = Swagelok female connector
D = Hollow plug, 1/8 inch NPT
(Drawing is 2X actual size; arrows show liquid flow)

Figure 7. Spray Tube for Dissolved Oxygen

then is broken up into a fine mist or spray when it hits the end of the hollow plug. The opening in the plug is much larger, about 1/8 inch. The spray is created only by the velocity of the liquid and the sudden contact with the end of the plug. There is no gaseous flow needed to create the spray, and so a constant pressure can be maintained within the pressure vessel.

The nozzle is mounted vertically in the upper part of a glass bottle, and fastened to the wall of a pressure chamber by a bulkhead fitting. Liquid is led (Fig. 8) from outside the chamber through this fitting. A two-way valve allows liquid to be sprayed into the bottle or to be removed by a delivery line D of 0.085 inch ID. A flow setting of 100 for the syringe gives a delivery time of about 11 seconds for the 100 ml to go through the nozzle (see Table I).

TABLE I

EFFECT OF PRESSURE AND SPRAY NOZZLE ON FLOW RATE OF SYRINGES

Syringe	Flow Control Setting	Exit Line		Opposing Pressure, psig	Flow Rate		Spray Time, sec
		Delivery	Spray		Advance, ml/sec	Retract, ml/sec	
Quench, 100 ml	100	+	-	0	10.0	12.5	
		-	+	0	9.6	--	10.4
	100	+	-	220	9.5	16.6	
		-	+	220	8.9	--	11.2
Quench	150	+	-	0	20	25.0	
		-	+	0	14.3	--	7.0
	150	+	-	220	19.2	27.8	
		-	+		13.3	--	7.5
Mix, 20.7 ml	100	+	-	0	1.09	1.38	--
		+	-	220	0.94	1.88	--

Note: It can be seen that advance rates are slower than retract rates; in the former, liquid has to be pushed out of the syringe and is a limiting factor; in retraction the syringe piston can move ahead of the liquid flow. Pressure slows down advance rates a little bit, but increases retraction rates a lot, pushing the liquid more rapidly through the inlet tubing. This is more noticeable at the slower flow rates, for both syringes.

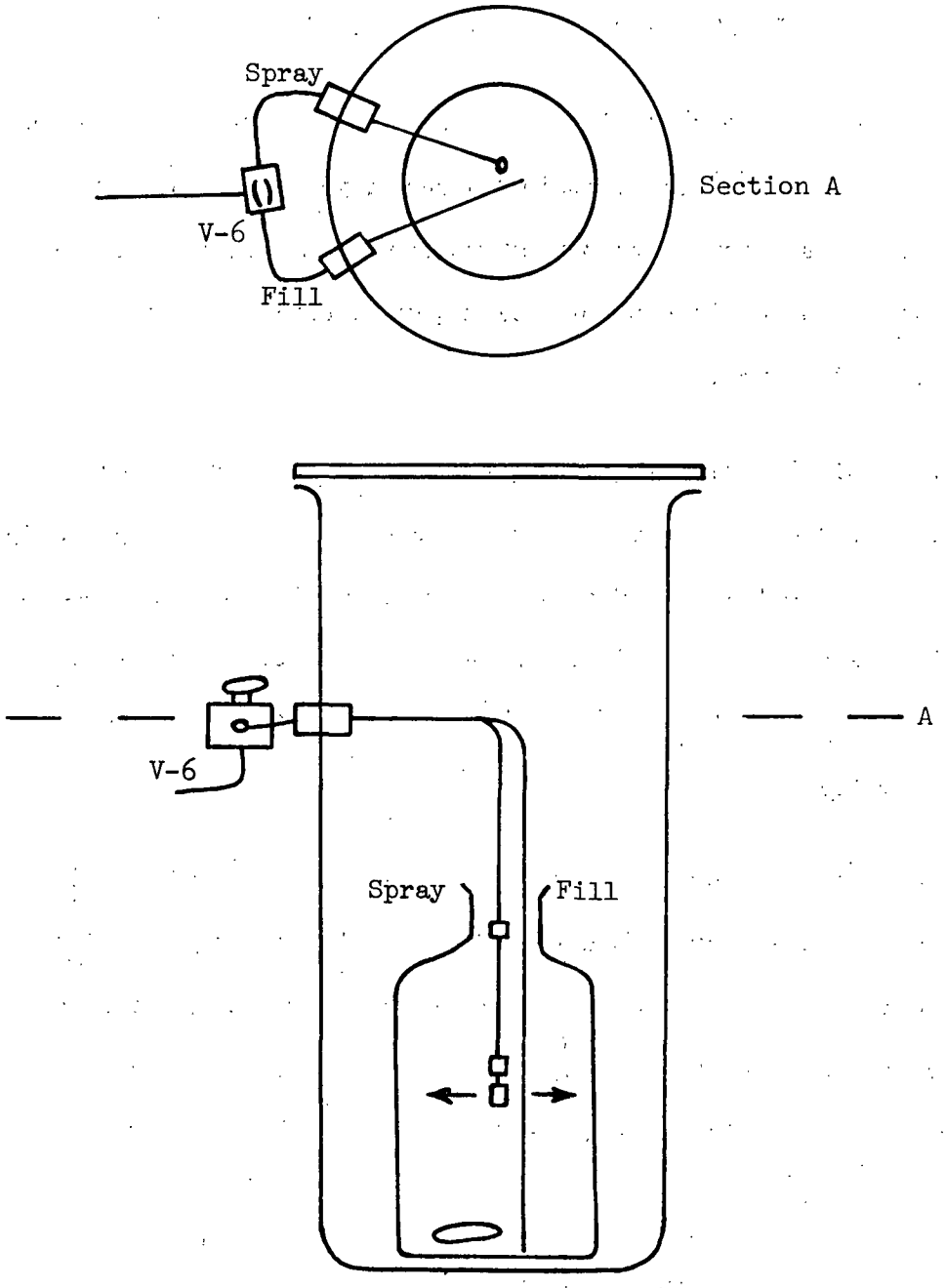


Figure 8. Arrangement of Spray and Fill Lines in Pressurized Oxygen Chamber

PREPARATION OF DISSOLVED OXYGEN UNDER PRESSURE

High concentrations of dissolved oxygen can be rapidly prepared by spraying water into a container maintained under high oxygen pressure. The amount of oxygen dissolved is about 70 to 80% of saturation at the oxygen pressure employed. The concentration is determined by passing a given volume of liquid through a Winkler trap under pressure.

Upon partially relieving the applied oxygen pressure within the container, various saturated aqueous solutions of oxygen can be prepared. Special precautions must be taken to ensure that rapid equilibrium is reached between the applied oxygen atmosphere and the oxygen in solution. This procedure gives a Henry's Law Constant at 26° of 0.0000127 m/liter/psi* which is the value reported at 25.9°C in the literature (9).

Using this procedure, the solubility of oxygen at 26°C in 0.1, 0.5 and 1.0N sodium hydroxide, sodium carbonate and sodium bicarbonate was determined. The results indicate little difference in solubility in dilute solution, while the solubility in 1N sodium hydroxide is about twice that in 1N sodium bicarbonate. Certain experimental uncertainties make the precise estimation of these quantities temporarily difficult.

EVALUATION OF THE SPRAY TECHNIQUE AND ANALYTICAL DETERMINATION

Four initial experiments were run on the preparation of dissolved oxygen in water at ambient temperatures of 18 to 20°C and 220 psig oxygen. The data are shown in Table II and Fig. 9. Most of the results showed that about 80% of the theoretical amount of oxygen was dissolved. In a few cases (Experiments 1 and 2)

*Moles/liter/pounds per square inch.

TABLE II

PREPARATION OF DISSOLVED OXYGEN UNDER PRESSURE

Expt.	Pressure of Oxygen, psig	Pressure of Oxygen, psia	Solution Technique: Spray, x	Solution Technique: Volume, ml	Solution Technique: Method	Stirring, hr	Oxygen Concentration: Found, ppm	Oxygen Concentration: Calcd., ppm	Oxygen Concentration: %
1	220	235	1	100	A		209	705	30
2	220	235	5	160	B		359	705	51
						1.0	296	705	42
	205	220				16	518	615	84
							526	615	86
							507	615	82
	180	195				24	451	585	77
3	220	235	1	100	C		529	705	75
							548	705	78
	220					0.5	582	705	83
4	220	235	1	200	C		412	705	58
	220	235				2	569	705	81
	150	165				0.5	410	495	83
	100	115				0.5	289	345	84
	50	65				0.5	146	195	75
	0	15				0.5	48	45	107

Note: Method A, solution sprayed in at flow setting of 150, C at flow setting of 100. Method B, 160 ml in chamber, 100 ml portions were withdrawn and sprayed back in at flow setting of 100; this was done 5 times.

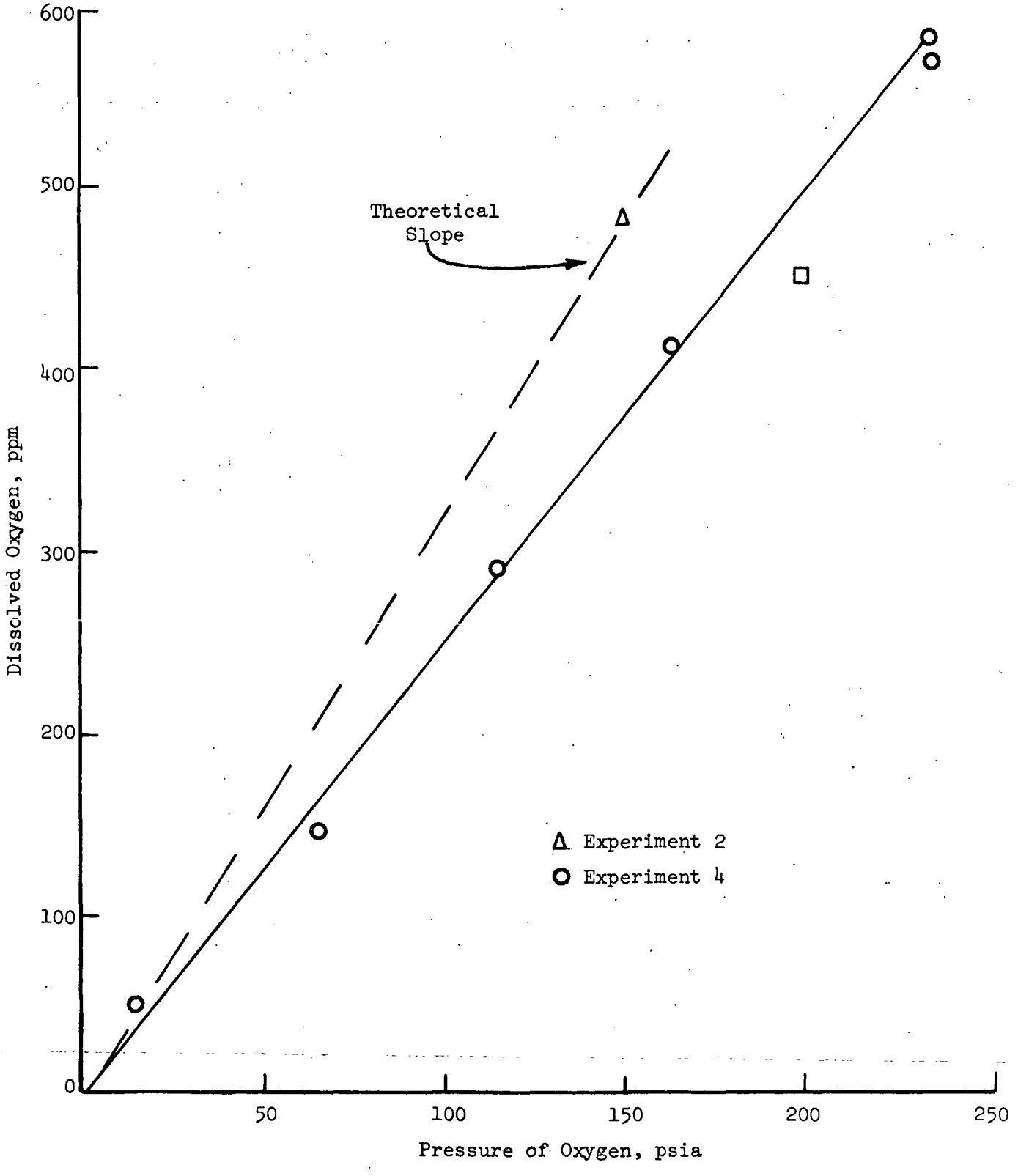


Figure 9. Linearity of Dissolved Oxygen Plotted Against Pressure

lower values were obtained and this may be attributed to poor technique. The spray technique at its best gave a high concentration of dissolved oxygen very quickly (Experiment 3) and stirring of the solution for 30 minutes or more thereafter gave a slight increase in concentration.

In a fourth experiment, the spray technique did not give a high value initially and stirring of the solution under pressure was needed to raise the oxygen concentration. Relieving the pressure to lower values did diminish the dissolved oxygen content, as shown in Fig. 9, but the technique still did not produce agreement with the predicted solubilities. This behavior was puzzling until it was realized that deviations from Henry's Law begin when the oxygen pressure is in excess of 100 psi and that many experimental variations could account for the present lack of agreement with the literature values below that pressure.

Another series of experiments was carried out to explore this possibility by saturating distilled water with oxygen at the limiting pressure for significant adherence to Henry's Law. The pressure was then diminished in a systematic manner to see if agreement with literature values could be obtained. The significance of the experiment was greatly enhanced by the fortuitous constant temperature (26 ± 0.5°C) of the laboratory and the equipment for the duration of the experiment. Future work will require precise temperature control to guarantee significant results.

The results shown in Table III indicate the variation in analyses encountered during the experiment. It is thought (but not proven) that most of the variation arises from the presence of small bubbles of gas within the tubing, interfering with the quantitative removal of samples for analysis. The data in Fig. 10 are compared with data for the solubility of oxygen in water at

25.9°C reported in the literature (9). The first point at 165 psia represents the quantity of oxygen initially dissolved for the experiment (about 70% of theory). Reduction of the oxygen pressure to 115 psia produces a saturated aqueous solution of oxygen at that pressure. Further reduction of the oxygen pressure showed levels of dissolved oxygen similar to those reported in the literature for 25.9°C. Henry's Law Constant thus obtained was similar to the literature value within experimental error.

TABLE III

THE SOLUBILITY OF OXYGEN IN DISTILLED WATER AT 26°C

Oxygen Pressure, psia	Iodine Titrated, ml	Solubility of Oxygen, moles/liter	Average
114.5	29.35	0.00917	
	29.05	0.00908	
	28.78	0.00899	0.00908 ± 0.00018
89.5	22.61	0.00707	
	21.78	0.00681	
	22.60	0.00706	0.00698 ± 0.00011
64.5	16.95	0.00530	
	17.05	0.00533	
	16.40	0.00513	0.00525 ± 0.00010
44.5	10.83	0.00338	
	10.60	0.00331	
	9.40	0.00294	
	10.20	0.00319	
	10.20	0.00319	0.00320 ± 0.00018

Precautions had to be taken to ensure that an equilibrium value for oxygen solubility was actually approached. Preliminary experiments indicated that, after the oxygen pressure had been reduced to a new value, a period of 2.5 hours was necessary before this goal was achieved. Stirring within the saturating vessel assisted to a significant degree, but the most effective method of achieving relatively constant analytical values in 40 min involved

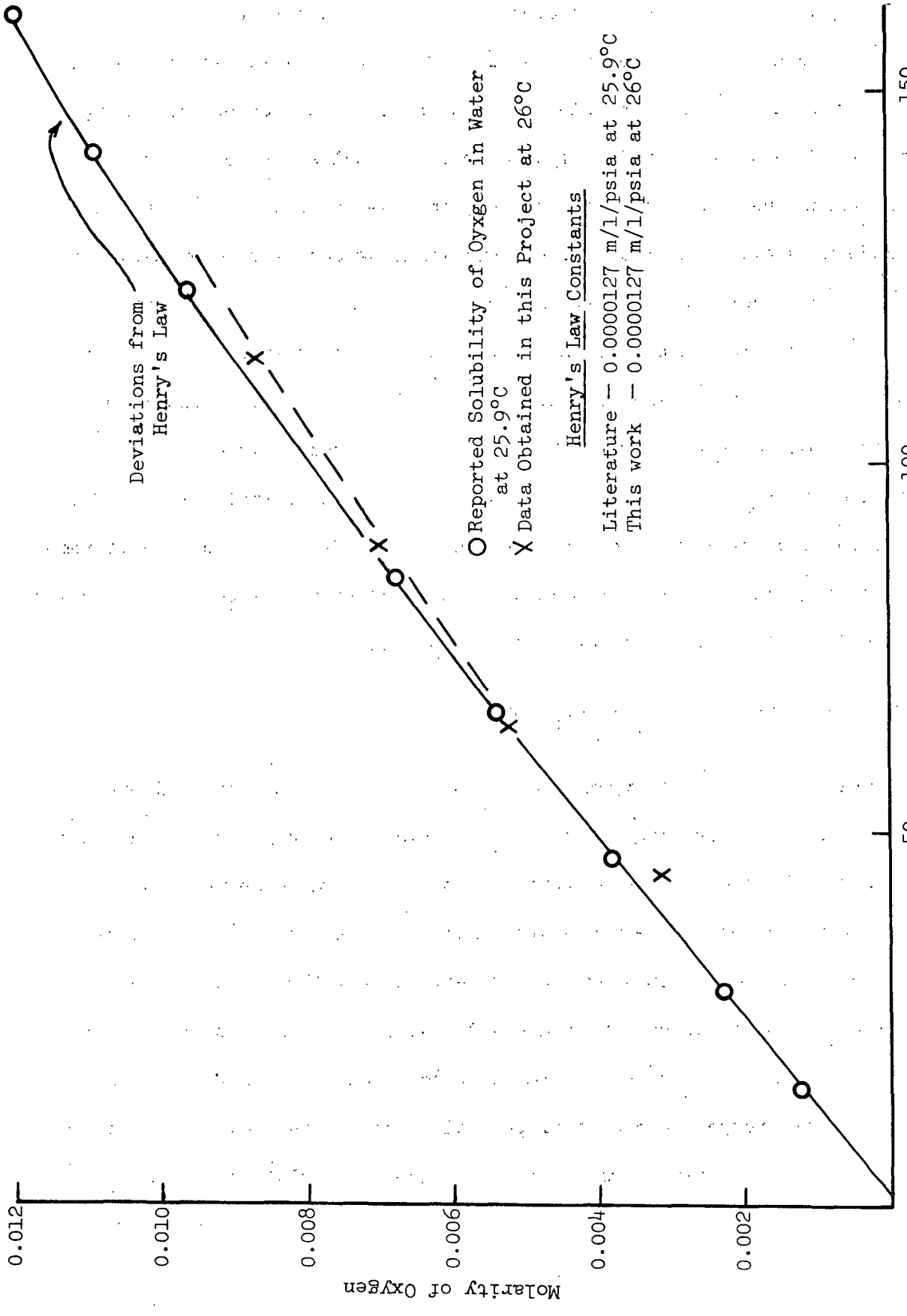


Figure 10. The Solubility of Oxygen in Distilled Water at 26°C

both stirring and pumping the oxygenated solution back and forth between the sampling syringe and the saturation vessel. If the pumping was started before 30 min standing and stirring, bubbles were sucked into the connecting tubing which were difficult to remove and led to erratic results. After 30 min the major portion of the "gas-off" was achieved, and the additional 5 to 10 min pumping made possible analytical values approximating equilibrium values. It is felt that the major source of error, apart from temperature uncertainties, is due to the accumulation of gas in the tubing and the syringe. The volume occupied by this gas will lead to a loss of liquid for analysis. Under the present conditions of operating the Winkler test, the undissolved oxygen is not given time to react with the Winkler solution and the overall effect of the bubbles is an apparent low dissolved oxygen content. With the addition of temperature control, it is felt that this apparatus and technique could be improved to give precise solubility data for gases in solvents.

THE SOLUBILITY OF OXYGEN IN SALT SOLUTIONS

The solubility of oxygen in salt solutions characteristic of oxygen pulping processes was investigated next. Once again, the major error in these experiments was the lack of temperature control, which was compounded by extreme daily weather variations. The temperature range from 22° to 29°C was approximately compensated for by applying factors derived from the variations of Henry's Law constant with temperature for oxygen and distilled water. Doubtlessly the changes in this constant for the several salt solutions would not be the same. The lack of proper temperature control probably obscures any small differences in the solubility of oxygen in water and in dilute salt solutions shown in Fig. 11 and Table IV.

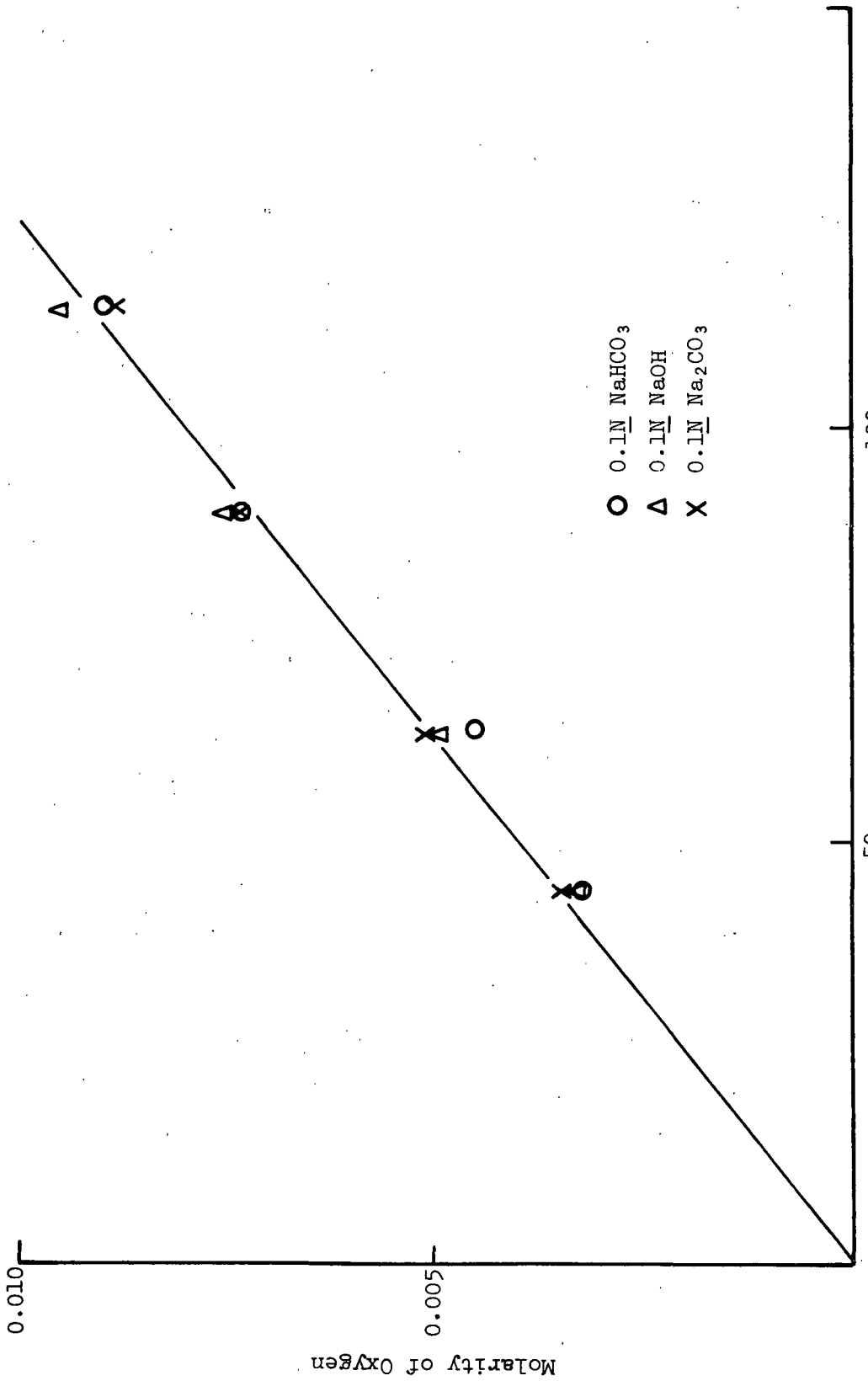


Figure 11. The Solubility of Oxygen in Dilute Salt Solutions at Different Pressures (Calculated to 26°C)

TABLE IV

SOLUBILITY OF OXYGEN IN 0.1N SALT SOLUTIONS,
CALCULATED FOR 26°C

0.1N NaOH		0.1N Na_2CO_3		0.1N $NaHCO_3$	
Oxygen Pressure, psia	Solubility[a]	Oxygen Pressure, psia	Solubility[a]	Oxygen Pressure, psia	Solubility[a]
114.5	0.00953	114.5	0.00898	114.5	0.00908
89.5	0.00759	89.5	0.00738	89.5	0.00745
64.5	0.00493	64.5	0.00513	64.5	0.00460
44.5	0.00325	44.5	0.00340	44.5	0.00327

[a] Triplicate analyses, expressed as moles/liter.

Solubility data were obtained (and adjusted to 26°C) for different pressures of oxygen in 0.5N solutions of sodium hydroxide, sodium carbonate and sodium bicarbonate. The carbonate solutions seemed to give more erratic results than the solutions of oxygen in sodium hydroxide. Since test samples of the carbonated, oxygenated solutions appeared to evolve greater quantities of gas than the caustic solutions when pumped into the atmosphere, it is presently speculated that a physical interference of uncertain origin upset the analysis. Despite the increased error, the results shown in Table V and compared in Fig. 12 indicate that increasing the carbonate content of a solution leads to decreased oxygen solubility. At 100 psia the solubility of oxygen in 0.5N sodium bicarbonate is only 73% of that in the corresponding strength of sodium hydroxide.

The solubility of oxygen in 1N solutions of sodium hydroxide, carbonate and bicarbonate is illustrated in Fig. 13 and Table VI. The bicarbonate solutions appear to give a greater experimental spread than the other solutions, but additional, more careful analyses are necessary to confirm this possibility. The

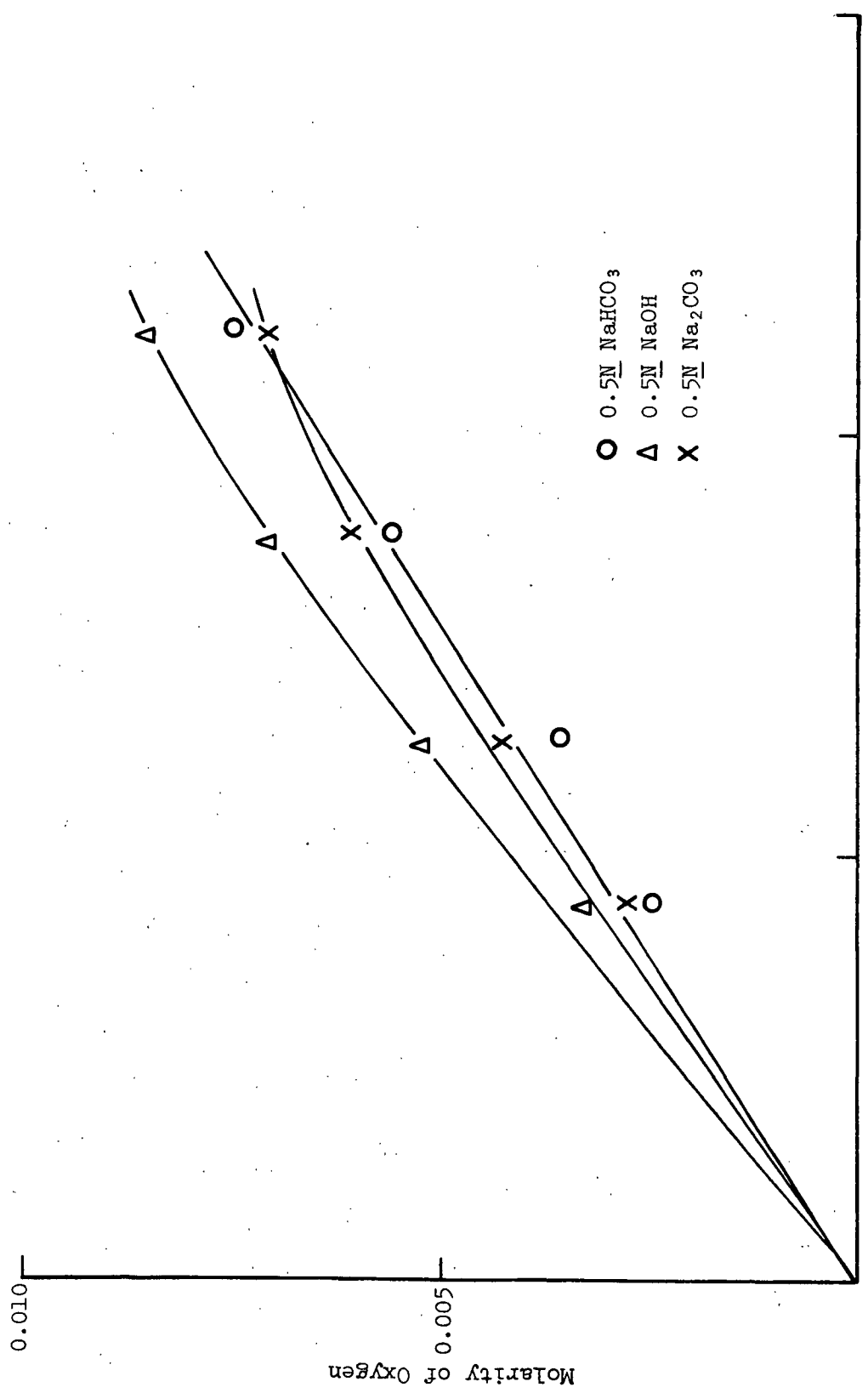


Figure 12. The Solubility of Oxygen in 0.5N Salt Solutions at Different Pressures (Calculated for 26°C)

TABLE V

SOLUBILITY OF OXYGEN IN 0.5N SALT SOLUTIONS, CALCULATED FOR 26°C

0.5N NaOH		0.5N Na_2CO_3		0.5N $NaHCO_3$	
Oxygen Pressure, psia	Solubility[a]	Oxygen Pressure, psia	Solubility[a]	Oxygen Pressure, psia	Solubility[a]
114.5	0.00816	114.5	0.00674	114.5	0.00703
89.5	0.00674	89.5	0.00572	89.5	0.00522
64.5	0.00503	64.5	0.00406	64.5	0.00331
44.5	0.00311	44.5	0.00254	44.5	0.00232

[a]Triplicate analyses, expressed as moles/liter.

TABLE VI

SOLUBILITY OF OXYGEN IN 1.0N SALT SOLUTIONS, CALCULATED FOR 26°C

1.0N NaOH		1.0N Na_2CO_3		1.0N $NaHCO_3$	
Oxygen Pressure, psia	Solubility[a]	Oxygen Pressure, psia	Solubility[a]	Oxygen Pressure, psia	Solubility[a]
114.5	0.00768	114.5	0.00726	114.5	0.00383
89.5	0.00632	89.5	0.00586	89.5	0.00371
64.5	0.00517	64.5	0.00413	64.5	0.00176
44.5	0.00316	44.5	0.00261	44.5	0.00116

[a]Triplicate analyses, expressed as moles/liter.

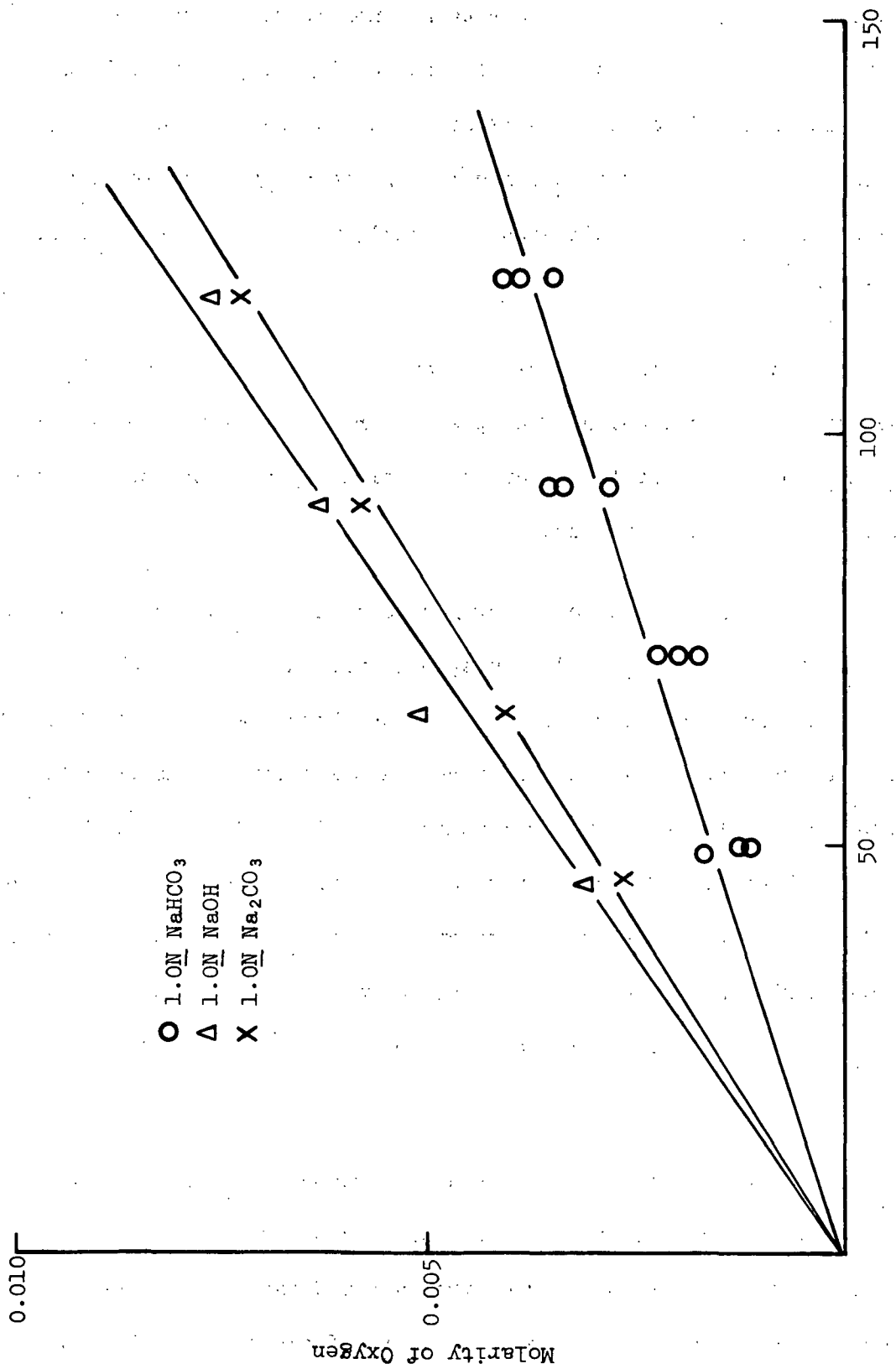


Figure 13. The Solubility of Oxygen in 1.0N Salt Solutions at Different Pressures (Calculated for 26°C)

comparisons are compounded by the uncertain temperature corrections necessary to approximate solubilities at 26°C. The solubility of oxygen in 1N sodium bicarbonate was only 50% of that in 1N sodium hydroxide at 26°C. After allowing for the increased solubility at the lower temperature, the corrected solubility of 60% demonstrated that the difference is real, not just a matter of differences in temperature.

The change in dissolved oxygen concentrations with increasing normality of the several solutions, and at four pressure ranges, are plotted in Fig. 14-16. It can readily be seen that the bicarbonate solutions show the strongest decrease in dissolved oxygen concentration.

The solubility behavior of oxygen found here is analogous to published behavior for other salts (10). At atmospheric pressure, the solubility of oxygen in 0.125N solutions of salts of strong acids and bases ranges from 95 to 98% of that found in pure water. In 1N solutions the solubility is about 80% of that found in water. In the present experiments (see Fig. 17) little difference was found in the solubility of oxygen in water or in salt solutions at lower pressures, and this is attributed to the relatively high experimental errors for the low concentrations measured. At higher oxygen pressures, significant differences are noted. It is likely that the analytical uncertainties in the apparatus can be eliminated.

The solubility of oxygen in sodium carbonate and bicarbonate solutions is similar to its solubility in ammonium chloride solution. In both cases the salt is formed from a weak ion (formed from a gas dissolved in water) and a strong counterion. For example, the solubility of oxygen in 0.125 and 1.0N ammonium chloride at atmospheric pressure and 25°C is about 40 and 12% of the

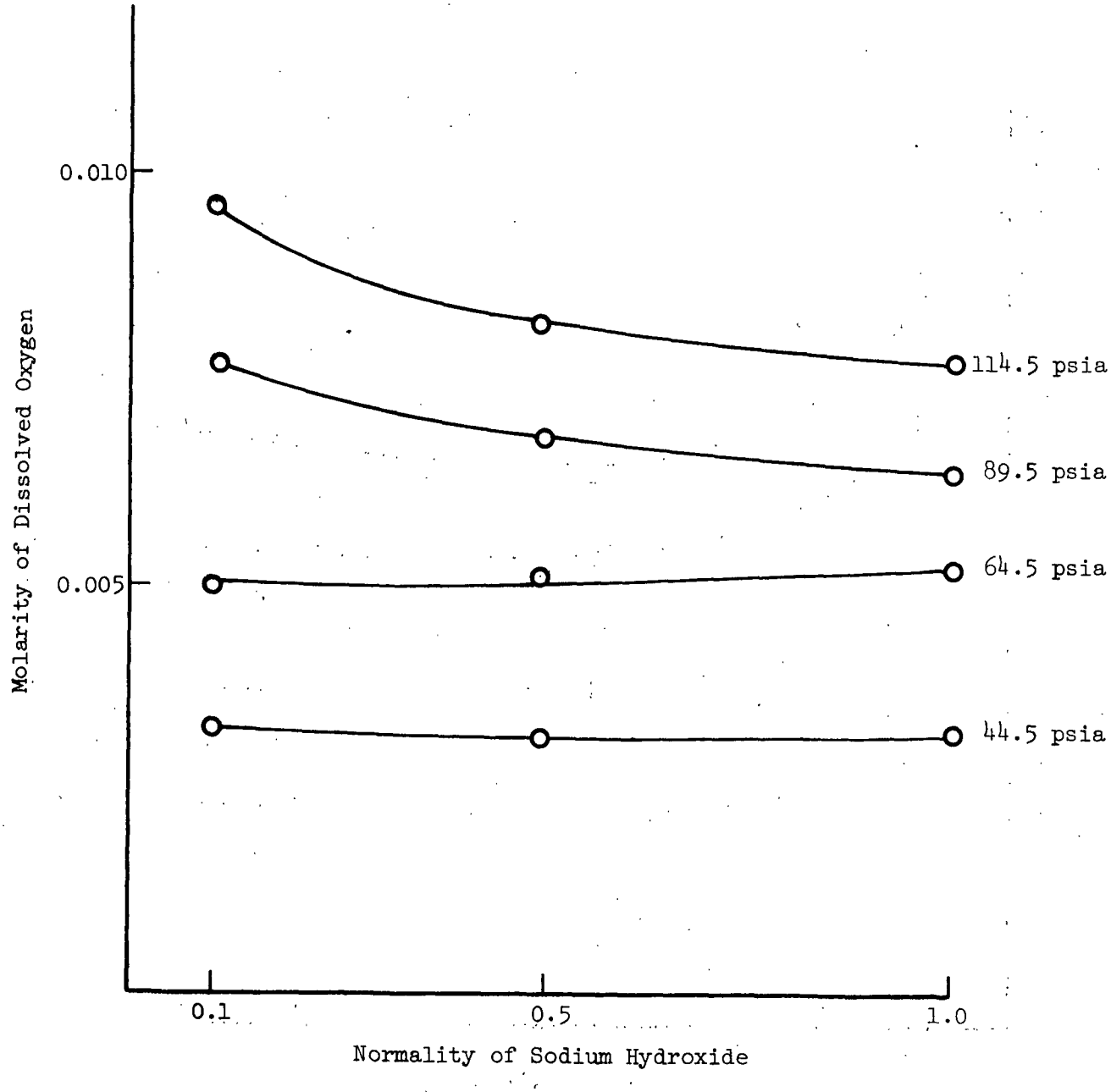


Figure 14. Decrease in Oxygen Solubility with Increasing Concentrations of Sodium Hydroxide

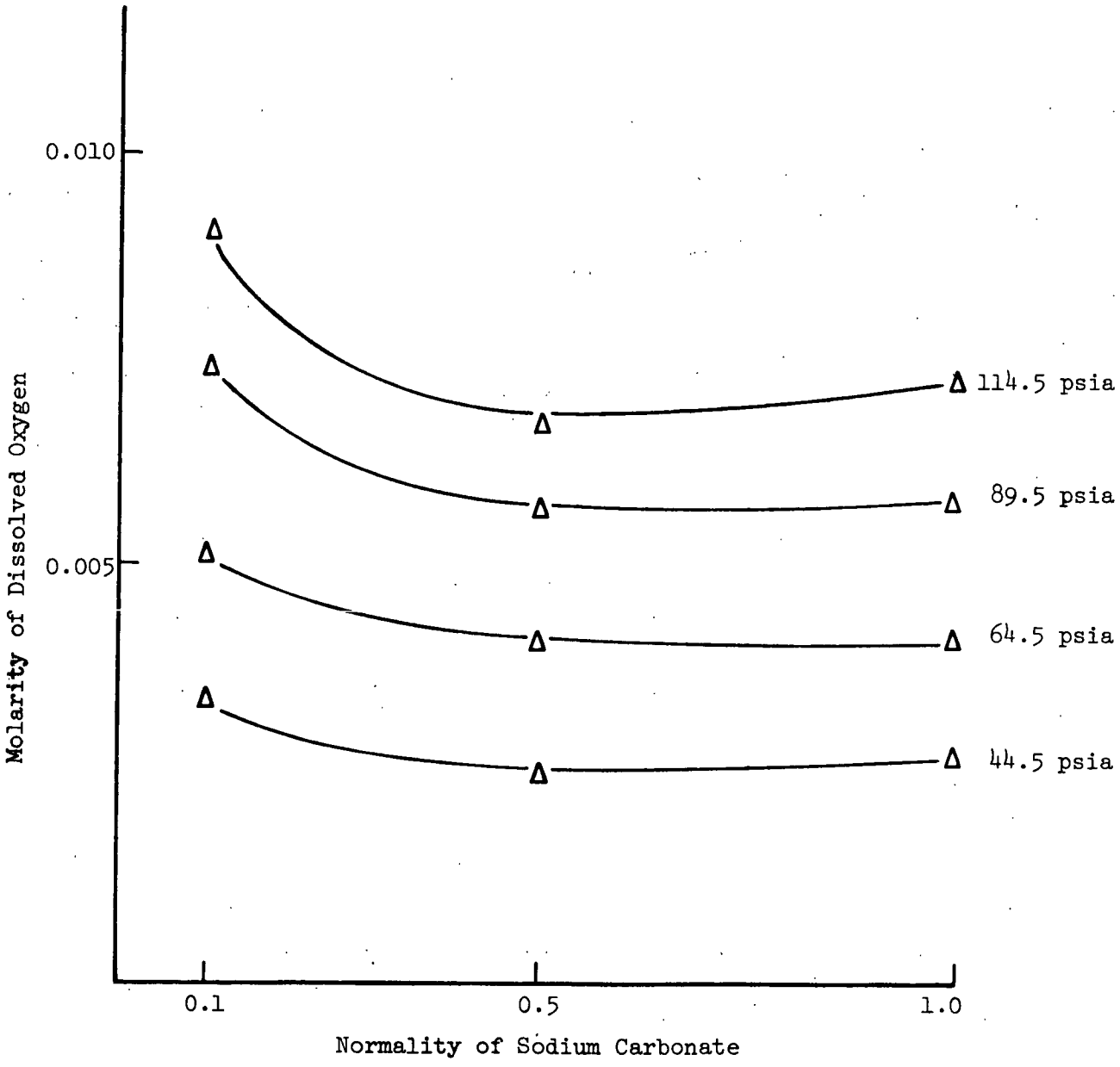


Figure 15. Decrease in Oxygen Solubility with Increasing Concentration of Sodium Carbonate

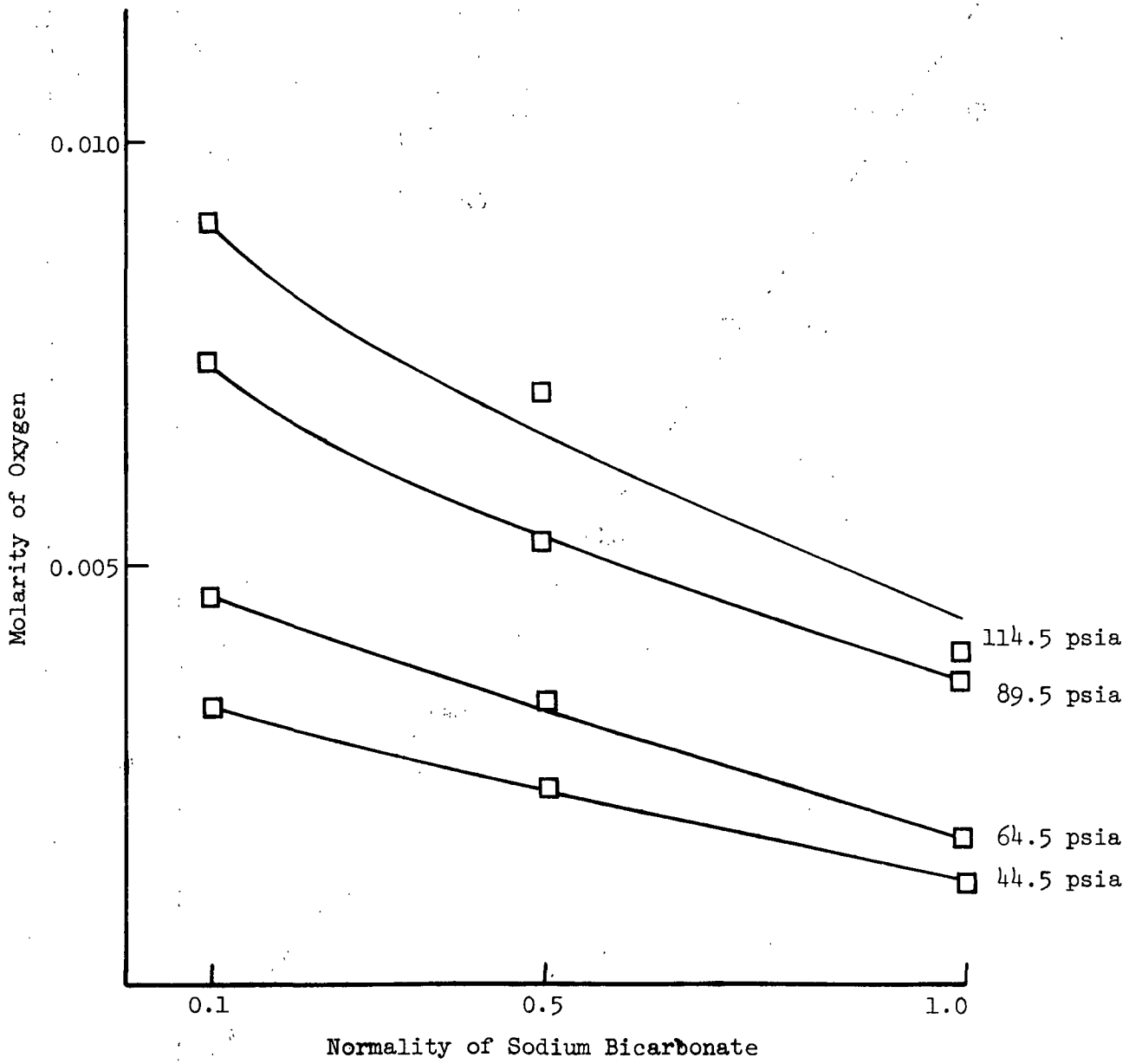


Figure 16. Decrease in Oxygen Solubility with Increasing Concentration of Sodium Bicarbonate

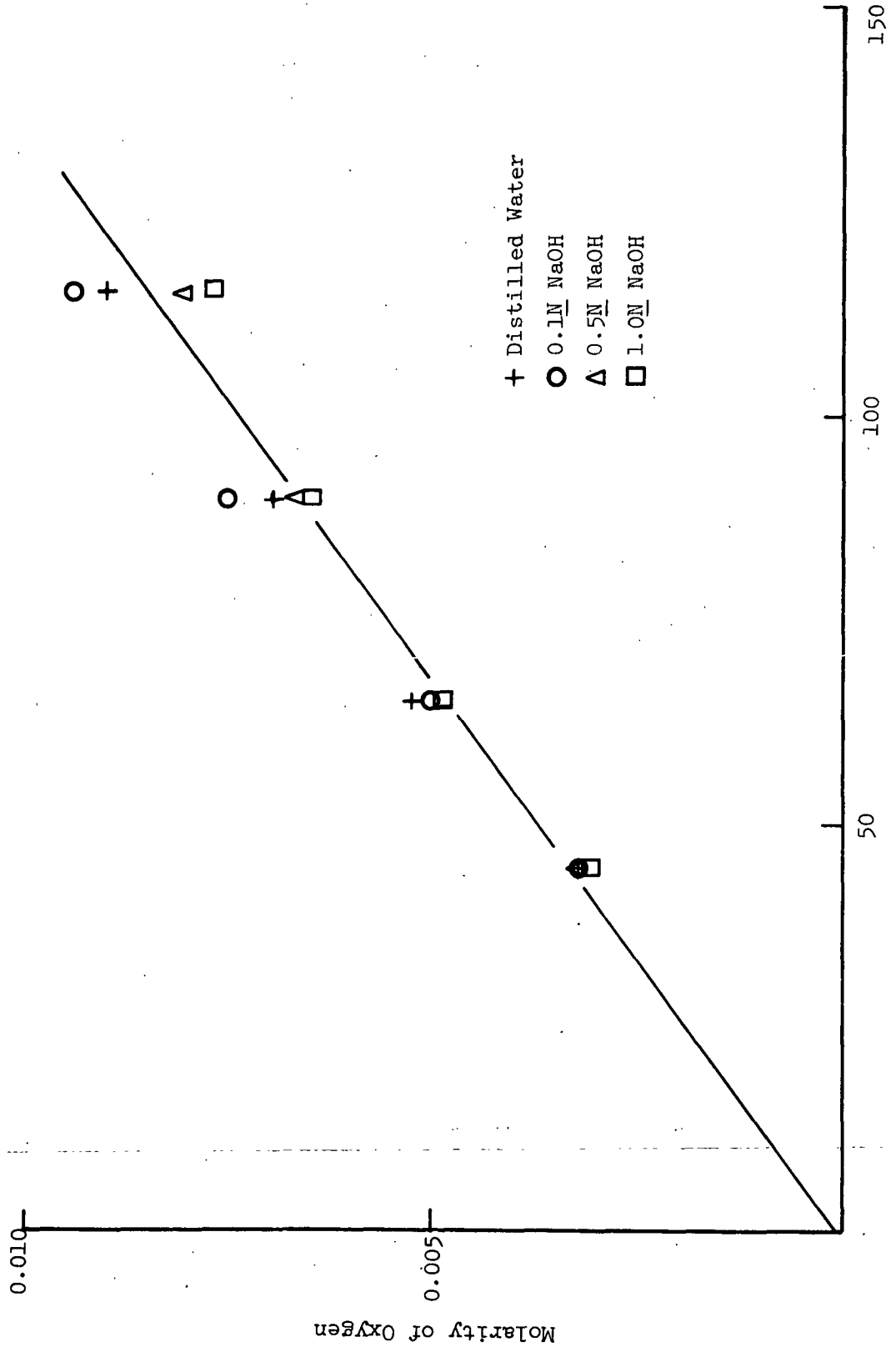


Figure 17. The Solubility of Oxygen in Various Concentrations of Sodium Hydroxide at 26°C

solubility in water (10). The complicating influence of carbonate on oxygen delignification noted by Samuelson (11) was rationalized by him to be an oxygen solubility problem in part, and these data tend to confirm his speculations. Further research at elevated temperatures is needed to prove this trend.

The results obtained here show that this oxygenation equipment can rapidly dissolve significant quantities of oxygen in aqueous solutions. The results indicate that, with proper modification and care, significant quantitative data may be obtained. These preliminary results indicate that carbonate ions (and perhaps even excess carbon dioxide) will have a significant depressing effect on oxygen solubility in aqueous solutions.

Preparation of Oxygenated Solutions

An empty 1000-ml narrow mouth bottle is placed in the pressure chamber, and the spray and feed lines fastened to the bulkhead fittings. The latter connect through valve V-6 to the flow reactor switchboard (Fig. 3). The latter is set up so that V-4 and V-5 are down and V-1 and V-2 up. This will connect only V-2 to V-6; the latter is set to connect with the spray line. (Valve V-3 is not involved in these operations.)

The oxygen chamber is then pressurized with oxygen to the desired pressure, and the 100-ml syringe at V-1 filled slowly (flow control setting 050) with water. V-1 is then turned down to connect the syringe with the dissolved oxygen line through valves V-1 and V-2. The syringe is then advanced at a flow rating of 100 to 150; any setting in this range will create a mist as the liquid is forced through the tubing shown in Fig. 7.

This procedure is repeated until 900 ml of the desired solution has been forced into the bottle. Magnetic stirring is conducted throughout the whole operation.

After analysis, the pressure of oxygen is reduced to the desired level and the solution allowed to stand for 30 min with stirring. The liquid is then pumped back and forth between the syringe and the oxygen chamber for 10 min to ensure rapid equilibrium between the gaseous and dissolved phases of oxygen.

During these movements of the mix syringe the Winkler trap has been flushed with nitrogen, filled with reagent, and pressurized with nitrogen. Valve V-5 is then turned up to connect the syringe with the trap. The syringe is advanced, driving the liquid into the trap.

THE EFFECT OF SODIUM CARBONATE SOLUTIONS ON THE DEGRADATION OF METHYL GLUCOSIDES BY OXYGEN AND SODIUM PEROXIDE

SUMMARY

This research has demonstrated that carbonate ion can participate in radical reactions leading to the very rapid decomposition of peroxides and to the degradation of glucopyranosyl rings. It is postulated that, during delignification reactions, the degradation of these rings occurs as a result of an interaction between hydroxyhydroperoxy radicals and the carbonate (or bicarbonate) ion to produce a carbonate radical which participates in further degradation of glucopyranosyl rings and other molecules. Both loss of viscosity and yield losses are expected to be the ultimate results of these degradations during pulping since the cleavage reactions can produce terminal carbonyl groups as well as carboxyl groups. The research indicates that the carbonate concentration as well as the pH are important factors in the reaction and suggests that optimum conditions of concentration of carbonate as well as pH will have to be maintained during the cook in order to optimize delignification reactions in carbonate solutions.

INTRODUCTION

Industrial interest in carbonate-oxygen pulping and bleaching arose from the realization that a relatively pollution-free recovery system can be developed based on a simplified soda recovery process (12). Another potential advantage was that carbohydrate degradation was less during oxygen delignification when the alkaline charge was reduced (13). This observation suggests that the buffering action of carbonated solutions might also have beneficial chemical effects due to lower pH as well as simplifying chemical recovery (14). These

interpretations were encouraged here by the results of Institute students Brooks (15), McCloskey (16), and Sinkey (17) showing the dependence of glycosidic bond degradation on caustic concentration and pH.

The results of bicarbonate and carbonate pulping obtained by Samuelson (11,14) were not up to his expectations since both the yield and pulp viscosity were adversely affected by the increasing presence of carbon dioxide during the reaction. Samuelson recognized the complex nature of the problem but could not account for all the adverse behaviors in terms of accessibility, oxygen solubility and changing pH due to carbonic acid (14).

Other anomalous behaviors occur during oxygen reactions in carbonated alkali such as the absence of peroxide in the reaction mixtures (18) which had previously been observed in soda-oxygen liquors (19). The effect of transition metal ions on pulp degradation in carbonate solutions was found to differ from their effects in alkali (20). Even the magnesium ion so beneficial to soda-oxygen pulping and bleaching had little effect on carbonate oxygen reactions (20) although potassium iodide was found to be a beneficial additive at lower pH levels (21).

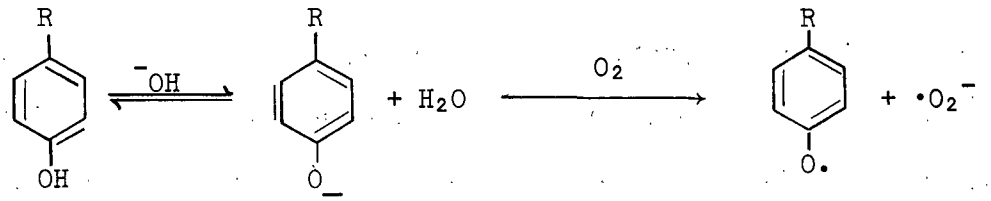
Project 3265 was developed to optimize yields after carbonate-oxygen delignification reactions by studying the effect of reaction parameters on the peeling and stopping reactions characteristic of the alkaline media in which the delignification is carried out. While the specialized equipment for this research was being set up, a literature survey and preliminary experiments were carried out in an attempt to clarify the actual experiments to be undertaken for the major phase of the research. This work attempted to look at the effect of oxygen and peroxide dissolved in both NaOH and Na_2CO_3 solutions on the reducing

ends and glycosidic bonds of cellulose model substances at lower temperatures than would be used in the final phase. Since it was immediately recognized that the two types of aqueous solutions have an effect on the nature of oxygen and peroxide dissolved in them, studies without glycosides present were also undertaken.

The research reported here is restricted to a cursory examination of factors considered to be important to delignification with oxygen in the presence of carbonate ion. Various factors which contribute to the loss of pulp viscosity and yield are discussed together with possible methods of minimizing these harmful effects.

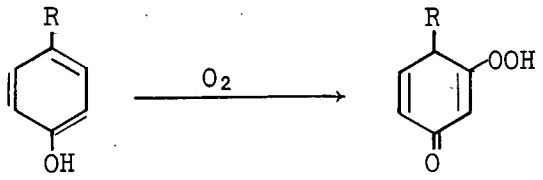
LITERATURE SURVEY

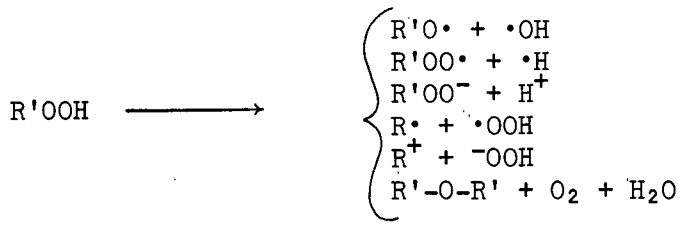
The results of the literature survey demonstrated that phenolic substances would react with peroxide to form a phenolate radical and perhydroxyl radical anion. Depending upon pH, this fragment could form the perhydroxyl radical as shown below (22).



$$\cdot O_2^- + H_2O \rightleftharpoons \cdot O_2H + {}^-OH$$

In carbonate solutions, phenolate ions would not exist and the reaction would take another direction. The organic peroxides formed under these conditions could react by a number of different mechanisms depending upon temperature, oxygen pressure, and concentrations (23).





Because of their phenolic character, lignin model substances were also found to behave in this manner (24,25). These reactions have been summarized in a schematic form by Gratzl, et al. (26) in Fig. 18. The inevitable by-product of these reactions is some form of reduced oxygen. Because of the quantum requirements of molecular oxygen, these reduced states are much more powerful oxidants than oxygen itself (27). Thus, the anomalous situation exists in which reaction products are more powerful oxidants than the original oxidant. Since this state of affairs does not occur elsewhere in pulping technology, care must be taken in extrapolating previous experience to this new pulping development.

The decomposition of hydrogen peroxide in aqueous solutions is difficult to understand despite many attempts at resolution reported in the literature. This difficulty arises because of the catalytic effect of trace contaminants (even in carefully purified systems), because uncontrolled induction periods make precise reproducibility (and, thus, interpretation) difficult and finally because of the lack of sufficient insight to design an effective investigative program to solve the problem. Two current nonconflicting theories which are often presented as conflicting theories in the literature are (24,28):

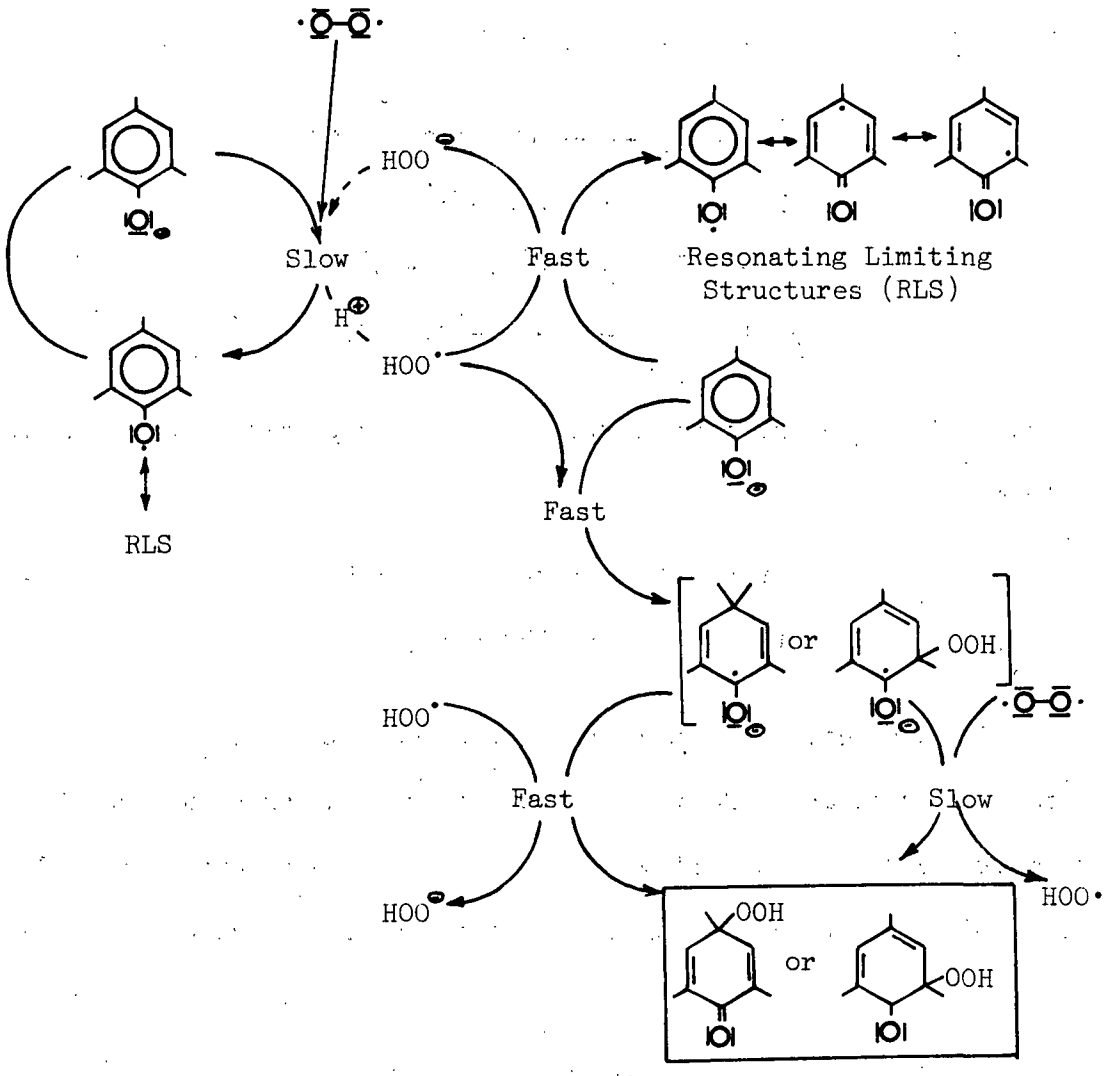


Figure 18. A Schematic Representation of the Separation of Lignin During Oxygen Delignification in Alkali (26).

1. The degradation of peroxide is related to the catalytic effect of the environment. In one case, transition metal ions were dealt with by Haber and Weis (28) and others (29) as follows:

$$M^n + H_2O_2 \longrightarrow M^{n+1} + OH + \cdot OH$$

$$\cdot OH + H_2O_2 \longrightarrow H_2O + \cdot O_2H$$

$$\cdot O_2H + M^{n+1} \longrightarrow M^n + O_2 + H^+$$

$$\cdot O_2H + H_2O_2 \longrightarrow \cdot OH + O_2 + H_2O$$

In another case, HBr (30) and even HI can be an active participant at certain acidic pH levels:

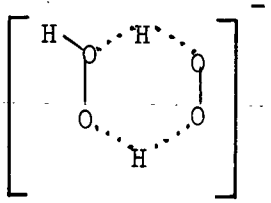
$$HBr + H_2O_2 \longrightarrow \cdot OH + H_2O + Br\cdot$$

$$Br\cdot + H_2O_2 \longrightarrow HBr + \cdot O_2H$$

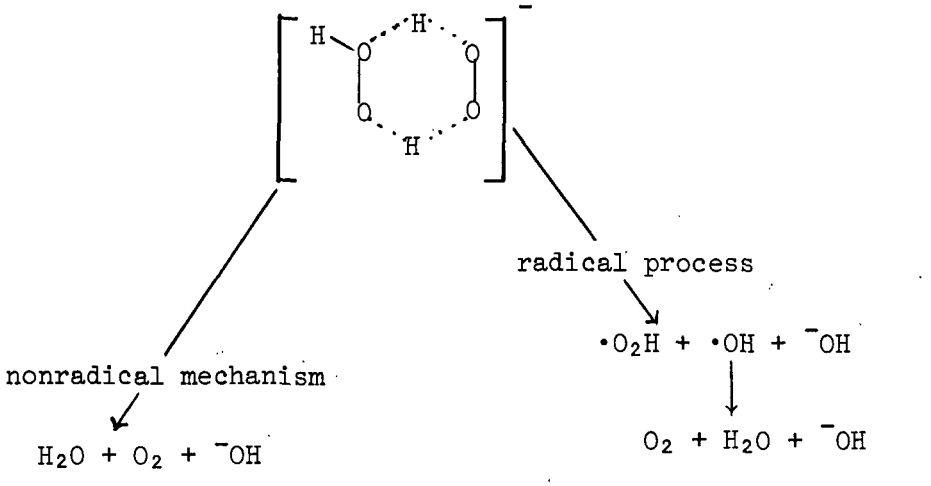
2. The degradation of peroxide is claimed related to the pH of its first dissociation constant. This type of decomposition has been shown to occur for peroxy acids and is used to rationalize why the decomposition of hydrogen peroxide often reaches a maximum at intermediate alkaline pH values (31-34).

$$H_2O_2 + {}^-OH \rightleftharpoons H_2O + {}^-O_2H$$

$${}^-O_2H + H_2O_2 \rightleftharpoons$$



The formation of the intermediate complex will reach a maximum when the concentration of hydrogen peroxide and perhydroxyl anion are equal. This occurs at pH 12 at 25°C (35). The subsequent decomposition of the complex is subject to controversy since some theories claim a 2-electron transfer is involved without the formation of free radicals whereas other theories claim that two single electron shifts occur with the liberation of radicals.



Whatever mechanisms are involved, the decomposition of peroxide is associated with its bleaching action (30,36) whether it is in acid or alkaline media. It is interesting to speculate that the reaction with woody material can involve the interaction of phenolate ions with hydroperoxy anions. By maintaining an environment of magnesium and silicate ion, the concurrent radical decomposition of peroxide is minimized and carbohydrate degradation is not appreciable (37).

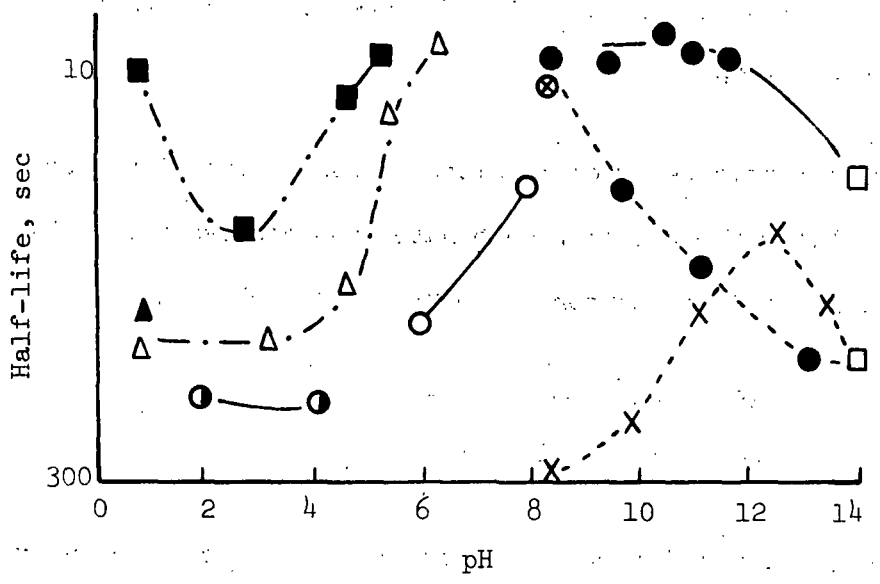
INVESTIGATIONS OF PEROXIDE STABILITY

Simple experiments were set up to compare the decomposition of hydrogen peroxide at different pH levels in the presence of different buffers. The literature suggested that at constant pH a dependence of peroxide decomposition on

different anions was possible (35,38). In these experiments, sodium borate was chosen as a convenient buffer to contrast with the carbonate buffers not only because of the similarity of the achievable pH buffering range but also because borate salts do not catalyze the decomposition of peroxide (39). The results were compared with those of Makkonen (40) and Cates, et al. (30,41) using other buffers and are shown in Fig. 19. Allowing for the temperature and concentration differences between the two, it is obvious that the effect of carbonate both in these experiments and in Makkonen's is to increase the rate of decomposition of hydrogen peroxide compared to sodium hydroxide.

The results of this research indicate that the instability of peroxide in carbonate buffers is not due to the first dissociation constant of the peroxide since the maximum rate of peroxide decomposition did not occur at pH 12.0. Makkonen (40) might have discovered this if he had studied the proper pH intervals or if he had compared buffers at the same pH with different catalytic effects on peroxide. On the other hand, the decomposition of hydrogen peroxide in borate buffers is probably related to the first dissociation constant of peroxide since a maximum rate of decomposition is observed close to pH 12.5. The slight difference between the observed pH and the anticipated pH (12.0) may be due to the limited number of experiments conducted, and to the likelihood that the high salt concentrations used here can alter the dissociation characteristics of the many salts in solution.

The literature indicates that both borate and carbonate salts can form peroxides of crystallization when hydrogen peroxide is present (39). Under suitable circumstance this could affect decomposition reactions if stable complexes existed in solution. Nevertheless, since a mixture of carbonate and borate salts at pH 8.5 still results in a rapid decomposition of hydrogen peroxide,



● Carbonate – hydroxide buffers
○ Monobasic phosphate – hydroxide
◑ Biphthalate – HCl
▲ KCl – HCl
△ NaCl – HCl
■ NaBr – HBr
X Borate – hydroxide
⊗ Carbonate – borate mixtures
□ NaOH

——— from Makkonen (40), 44 mM H_2O_2; ∿0.1M Buffer solution, 60 and 82°C

---- This research, 0.17 mM H_2O_2 ∿1.25M Buffer at 25°C

-·-·-· Estimated from the data of Cates et al. (41)

Figure 19. The Half-lives for the Decomposition of Buffered Hydrogen Peroxide as a Function of pH and Buffers

the predominant mechanism involved in this comparison of the two buffers is likely to be a destabilization action as a result of carbonate ion rather than a stabilizing action on the part of the borate salt.

The mechanism for this behavior remained obscure until it was observed in the literature (42) that carbonate or bicarbonate ions can react with hydroxyl radicals during pulse radiolysis of carbonate solutions as follows:

$$\cdot OH + CO_3^{=} \longrightarrow {}^{-}OH + \cdot CO_3^{-}$$

$$\cdot OH + HCO_3^{-} \longrightarrow H_2O + \cdot CO_3^{-}$$

The rate of the following termination reaction was also followed in these radiolysis experiments

$$\cdot OH + \cdot CO_3^{-} \longrightarrow \text{products [probably } CO_3^{=} + O_2]$$

Thus, it becomes possible to account for the decomposition of peroxide as a chain mechanism in which the carbonate acts as a carrier during the propagation stage of the reaction.

Many pathways are possible, especially since the carbonate radicals might react with other molecules or themselves in termination reactions involving the oxidation or reduction of the carbon involved. Since it was not possible to detect carbon monoxide, oxalic acid and formic acid after the decomposition of hydrogen peroxide by sodium carbonate, many mechanisms can, therefore, be eliminated from consideration leaving the following possibility:

1. Initial stage: due to catalytic decomposition initiated by trace contamination:

$$H_2O_2 \xrightarrow{\text{catalysis}} \cdot OH + \cdot O_2H, \text{ etc.}$$

2. Generation of carbonate radical:

$$HCO_3^- + \cdot OH \longrightarrow H_2O + \cdot CO_3^-$$

3. Propagating stage: reaction of peroxide with carbonate radical to give perhydroxyl radical: $H_2O_2 + CO_3^- \longrightarrow HCO_3^- + \cdot O_2H$

: decomposition of peroxide by perhydroxyl radical with the liberation of more hydroxyl radical:

$$H_2O_2 + \cdot O_2H \longrightarrow H_2O + O_2 + \cdot OH$$

4. Limiting reactions: as the pH increases, more perhydroxyl anion is formed. The reaction is probably slowed since now two electron-rich particles must overcome repulsions in order to react:

$$HO_2^- + \cdot O_2H \longrightarrow {}^-OH + O_2 + \cdot OH$$

$$HO_2^- + \cdot CO_3^- \longrightarrow CO_3^{=} + \cdot O_2H$$

: the generation of the carbonate radical is also probably slowed when the pH increases for the same reason.

$$HCO_3^- + \cdot O^- \longrightarrow {}^-OH + \cdot CO_3^-$$

$$CO_3^{=} + \cdot O^- \longrightarrow O^{=} + \cdot CO_3^-$$

5. Terminating reactions:

$$\cdot CO_3^- + \cdot O_2H \longrightarrow CO_3^{=} + O_2$$

$$\cdot OH + \cdot OH \longrightarrow H_2O_2$$

$$\cdot O_2H + \cdot CO_3^- \longrightarrow HCO_3^- + O_2$$

The shape of the peroxide decomposition curve in alkaline media buffered with carbon dioxide conducted here and shown in Fig. 19 can be rationalized on the basis of the reactions described above. The carbonate salts act to promote

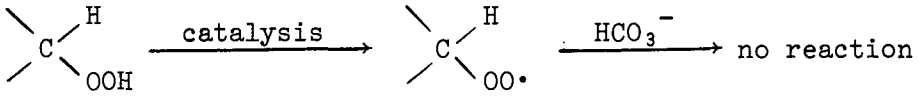
the propagation stage of the decomposition of peroxide and a comparison of these data with that of Makkonen suggests that the effect is not catalytic but depends upon the concentration of dissolved carbonate as well as on pH. Limitations of time (and budget?) necessitate deferring the proof of this speculation and resolving the differences between this research and that of Makkonen. Since the decomposition slows with increasing pH probably both carbonate ion ($CO_3^=$) and the perhydroxyl ion (O_2^-) are less reactive propagating species as suggested above. It is also possible that the radical $\cdot O^-$ is also less reactive for the same reasons.

$$\cdot OH + {}^-OH \qquad \cdot O^- + H_2O$$

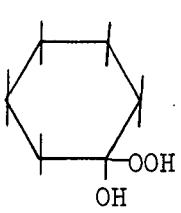
Since the presence of carbonate salts affects the rate of decomposition of peroxides, it is likely that its presence must also affect the reaction of organic molecules either directly by participating in degradative mechanisms or indirectly by destroying otherwise harmful peroxidic intermediates. If the destruction of peroxidic intermediates is by nonradical processes (unlike the radical process described above), carbonate should minimize the degradation of other organic substances by peroxide. On the other hand, if radical processes are involved, the reaction of other organic substances may or may not be enhanced depending upon the nature of the reactions and the equilibria involved.

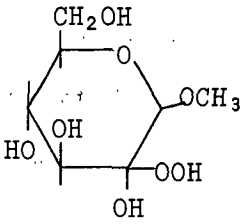
THE EFFECT OF CARBONATE SALTS ON THE DEGRADATION OF ORGANIC SUBSTANCES BY RADICAL PROCESSES

The radical decomposition of cyclohexanol peroxide in the presence of carbonate ion has been shown by Denisov, et al. (43) to be slowed suggesting the bicarbonate ions are a negative catalyst. This conclusion may be extrapolated to other alkyl peroxides of similar configuration.

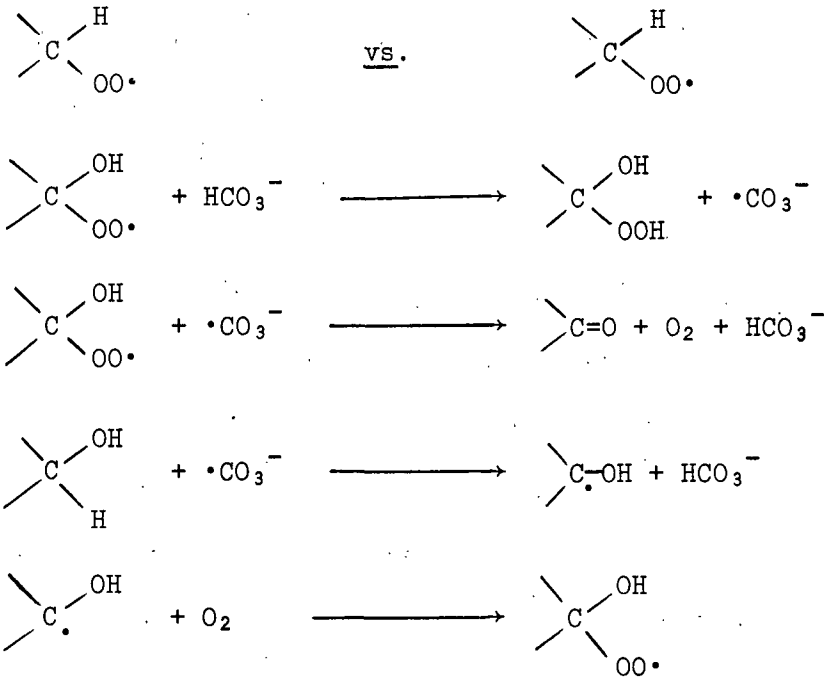


Cyclohexanone peroxide behaves in a different manner and is decomposed more rapidly in the presence of bicarbonate ion. Cyclohexanone peroxide is a mixture of peroxides some of which have structural configurations similar to the hydroxy-hydroperoxides postulated to exist as intermediates during both oxygen and peroxide degradation of cellulose model substances (44,45).





They also found that a mixture of cyclohexanone peroxide and cyclohexanol catalyses the decomposition of the latter when bicarbonate ion is present and the results were rationalized as follows by making use of the different reactivities of the two functional groups:



This literature review indicates that the degradation of cellulose should be adversely affected by carbonate ions during both oxygen and peroxide delignification reactions and that otherwise inert substances (extractives) as well as reactive components will be affected. The interaction between carbohydrate and oxygen will not occur rapidly unless the oxygen has been reduced to a more reactive state capable of interacting with the carbonate ion. This reaction should be very slow during cellulose or viscose alkali-aging reactions and very rapid during delignification reactions where more peroxides, including organic peroxides, are formed and behave as intermediates to react with the carbonate ion. The chain reactions initiated by this process should be very sensitive to damping by scavengers such as the iodide ion. Whether this observed phenomenon is due to the decomposition of the peroxides or certain intermediate radicals is not yet known. The observation that iodide ion is not an effectual stabilizer in O_2, sodium hydroxide reactions is consistent with this rationalization.

THE EFFECT OF CARBONATE SALTS ON OXYGEN-INITIATED OXIDATIONS

The effect of carbonate solutions on the degradation of MBG by peroxide was studied using modifications of the techniques employed by Weaver (34) to study the degradation of methyl β-D-glucopyranoside by alkaline peroxide in the presence of metal catalysts (44). The reactions were carried out in a polypropylene reactor at 60°C for varying periods of time employing 10 mM MBG, 1 mM $MgSO_4$, and different pH levels using NaOH, Na_2CO_3, and $NaHCO_3$ buffers. The samples removed at different time intervals were analyzed for hydrogen peroxide, organic peroxide and one portion of them was reduced with Na_2SO_3. It was next deionized with Dowex 50W-X8, neutralized to pH 7, and evaporated to dryness. The reaction products in the sample were detected by GLC after preparing trimethyl

silyl derivatives by standard procedures. Because of the complex nature of the products, quantitative analyses were not carried out in order to limit the expense and time involved.

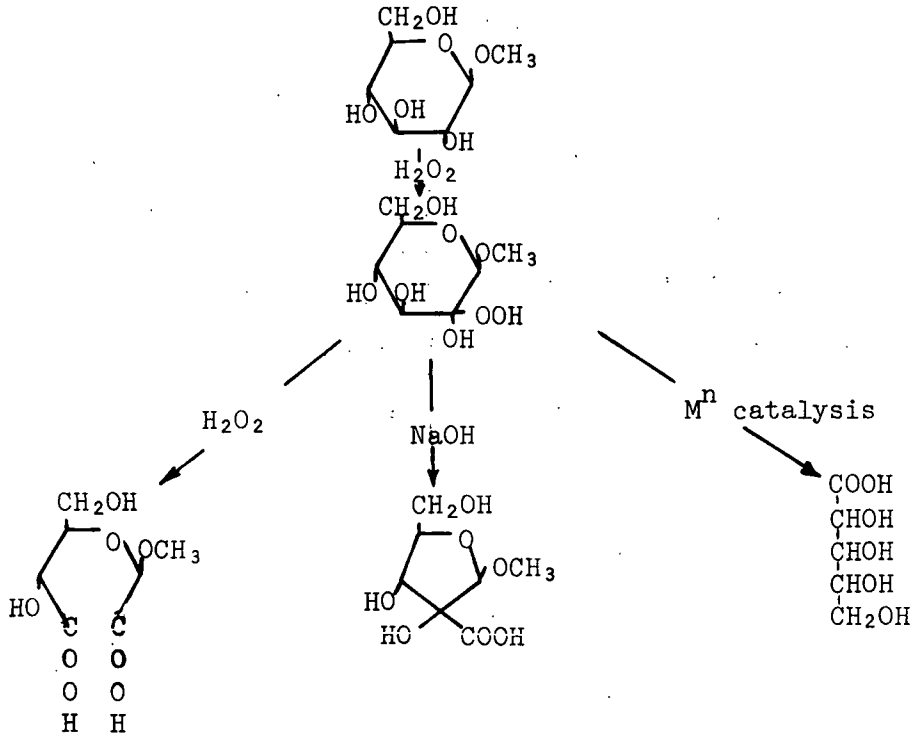
A qualitative examination of the reaction products is given in Table VII and the products and their distribution (not described in detail in Table VII) seem to be generally similar to those reported by Weaver for the oxidations with alkaline peroxide in the presence and absence of magnesium ion (44). It must be emphasized that this product analysis is not quantitative nor was any attempt made to establish the identity of any reaction products other than MBG and arabinonic acid. Nevertheless, low molecular weight products will tend to fall in one characteristic region of the chromatogram whereas products such as the 2-C-carboxy degradation products will fall in a chromatographic location that differs from the above products and from the anticipated dicarboxylic acid derivatives (44).

TABLE VII

QUALITATIVE DESCRIPTION OF GLC PATTERNS OF MBG DEGRADED BY ALKALINE PEROXIDE SOLUTIONS

Alkali	$MgSO_4$	Order of Rate of Degradation of MBG	$t_{1/2}$ of H_2O_2	Maximum Organic Peroxide, relative units	Product Pattern
NaOH	+	1	41 hr	0.015	Arabinonic acid formed, many small fragments
NaOH	-	2	12 hr	0.040	Arabinonic acid formed, many small fragments
Na_2CO_3 (pH, 11.7)	+	2	7 min	Trace?	Arabinonic acid and possible dicarboxylic acid in greater quantity than detected above
$NaHCO_3$ (pH, 9)	+	3	4 min	0	No arabinonic acid but different dicarboxylic acid and fewer low molecular weight fragments in greater quantity than above

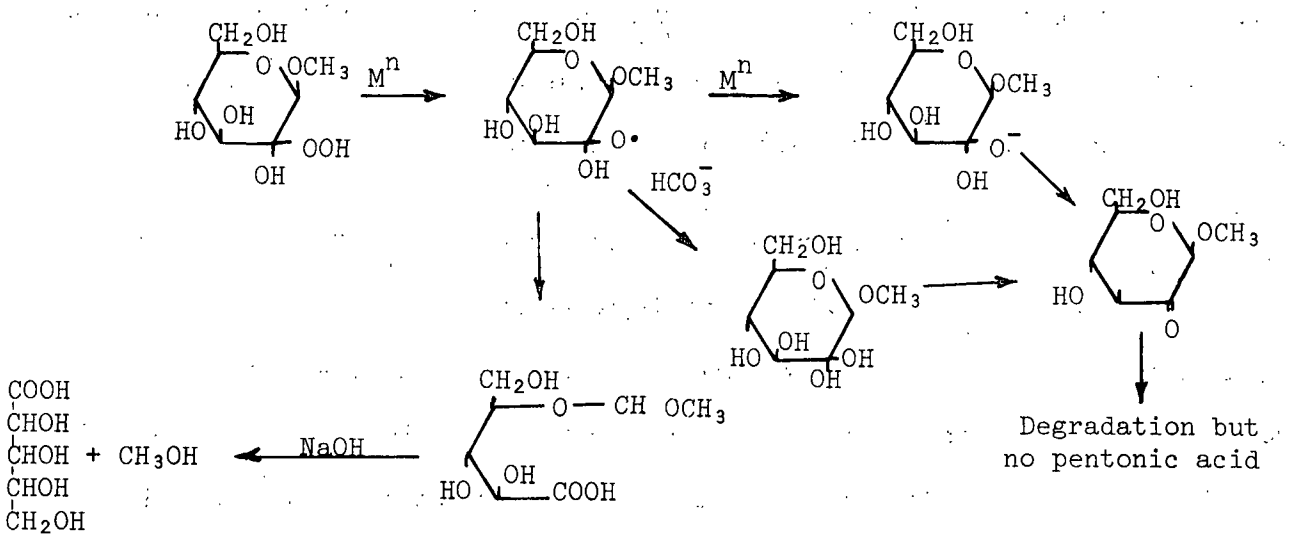
This generalized approach is useful since each classification corresponds to the postulated decomposition routes available to the intermediate organic peroxides formed in the reaction as shown below:



Dicarboxylic Acids 2-C-Carboxy Derivatives Pentonic (Arabinonic) Acids

In practice, it was difficult to make positive statements about the pattern in the 2-C-carboxy derivative region because a number of other products, including trace quantities of organic peroxides, lactones and MBG itself occur close together. The pentonic acid fraction is readily located and, by comparing it with controls, it was apparent that very little, if indeed any, pentonic acid was detected when a sodium bicarbonate buffer was employed. Pentonic acids were detected in the other 3 reactions, however. This observation does not imply a fundamental difference in the reaction mechanism between carbonate and bicarbonate buffers but rather a manifestation of the different concentrations of carbonate and bicarbonate ions in the two buffers. Thus, the excess bicarbonate

ions could participate further in the reaction as does excess transition metal ions to eliminate arabinonic acid. These types of reactions might be as follows:



In the more alkaline pH, characteristic of sodium carbonate solution, alkaline degradations of the keto group would occur to a greater extent than in bicarbonate solutions. In the latter solutions, the peroxidic oxidations of the intermediate ketone would next occur to a relatively greater extent than in the carbonate solutions. This is indeed the way in which the qualitative GLC patterns can be interpreted but careful quantitative analysis is needed to prove this speculation. The few, but larger, quantities of low-molecular weight acids detected after bicarbonate buffered oxidations may be the result of fewer intermediate reaction products leading to fewer final reaction products.

Not only does carbonate influence the direction the carbohydrate degradations undergo, but it also alters the rate of degradation of the carbohydrate material. In general, by comparing the size of the residual GLC area of the MBG isolated from the oxidations at different times but under conditions which should contain equal quantities of starting MBG, it was concluded that the degradation in sodium bicarbonate occurred more rapidly than in either carbonate

or sodium hydroxide. The degradation of MBG using sodium carbonate buffer occurred at about the same rate as unstabilized (no magnesium ion) degradations in sodium hydroxide. Further experiments are obviously necessary to verify these observations and to resolve the unexplored effect of the concentrations of carbonate and bicarbonate ions on the degradation independent of the applied pH.

Another series of experiments was conducted to verify the postulate that carbonate solutions will affect the degradation of carbohydrates during oxygen reactions as well as during peroxide oxidations. In these, methyl α-D-glucopyranoside (MAG) was chosen as a model because of a temporary shortage of MBG. The researches of Sjöström and Malinen (46) suggest no significant differences in interpretation should result from this substitution of one model substance for another. The results shown in Fig. 20 confirm that the effect of caustic concentration on the degradation of MAG during oxygen-alkali reactions is the same as the effect on MBG studied earlier (16,17).

Figure 21 contains plots demonstrating that the rate of reaction of MAG is altered by altering the pH of the oxidizing system. Brooks has also observed this when he compared the rate of degradation of MBG by oxygen in caustic and carbonate solutions (15). The interpretation of the plots in Fig. 21 is based on the assumptions that the pH is more closely related to the ratio of the concentrations of the salts and ions participating than it is in the absolute concentrations of the components. The assumption is also made that no drastic alteration of the pH occurs when the carbonate-rich solutions are heated to 120°C. The behavior of MAG in sodium carbonate solutions shows that even at pH 11.5 significant degradation can occur. More important, the plots demonstrate that altering the quantity of buffering carbonate used to achieve the pH has as great an effect on glycoside bond degradation as pH itself. Since a basic hypothesis of these

theoretical delignification studies is that polysaccharides are relatively stable in the presence of oxygen but are rapidly decomposed by peroxides and their equivalents in the reaction medium, a source of peroxide must be provided. The particular pH levels used in these experiments were chosen in order to provide a significant quantity of hydrogen peroxide to act as the reactive intermediate with the carbonated solutions.

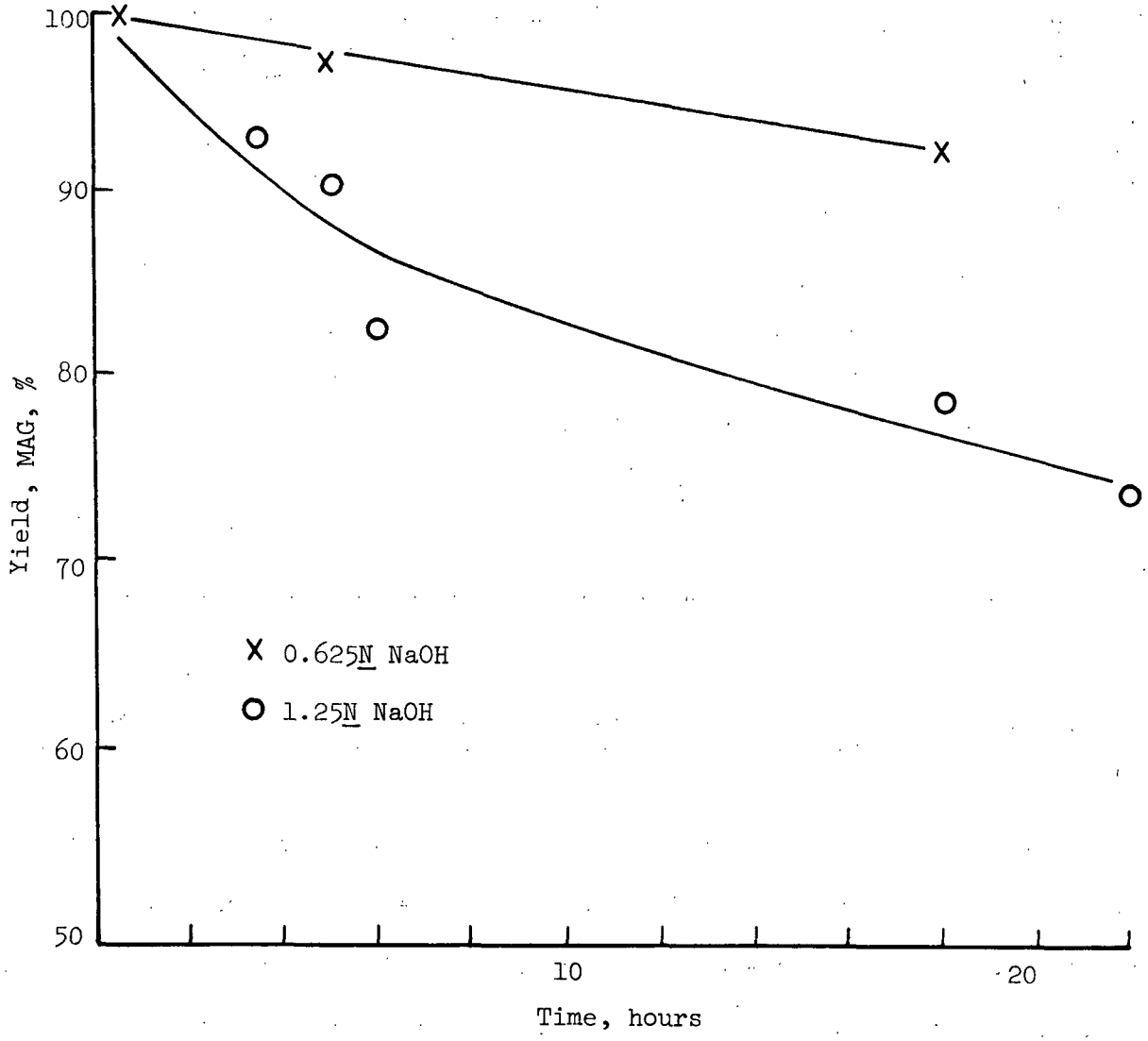


Figure 20. The Degradation of MAG with Time of Reaction in NaOH Solutions at 120°C and 100 psig O_2

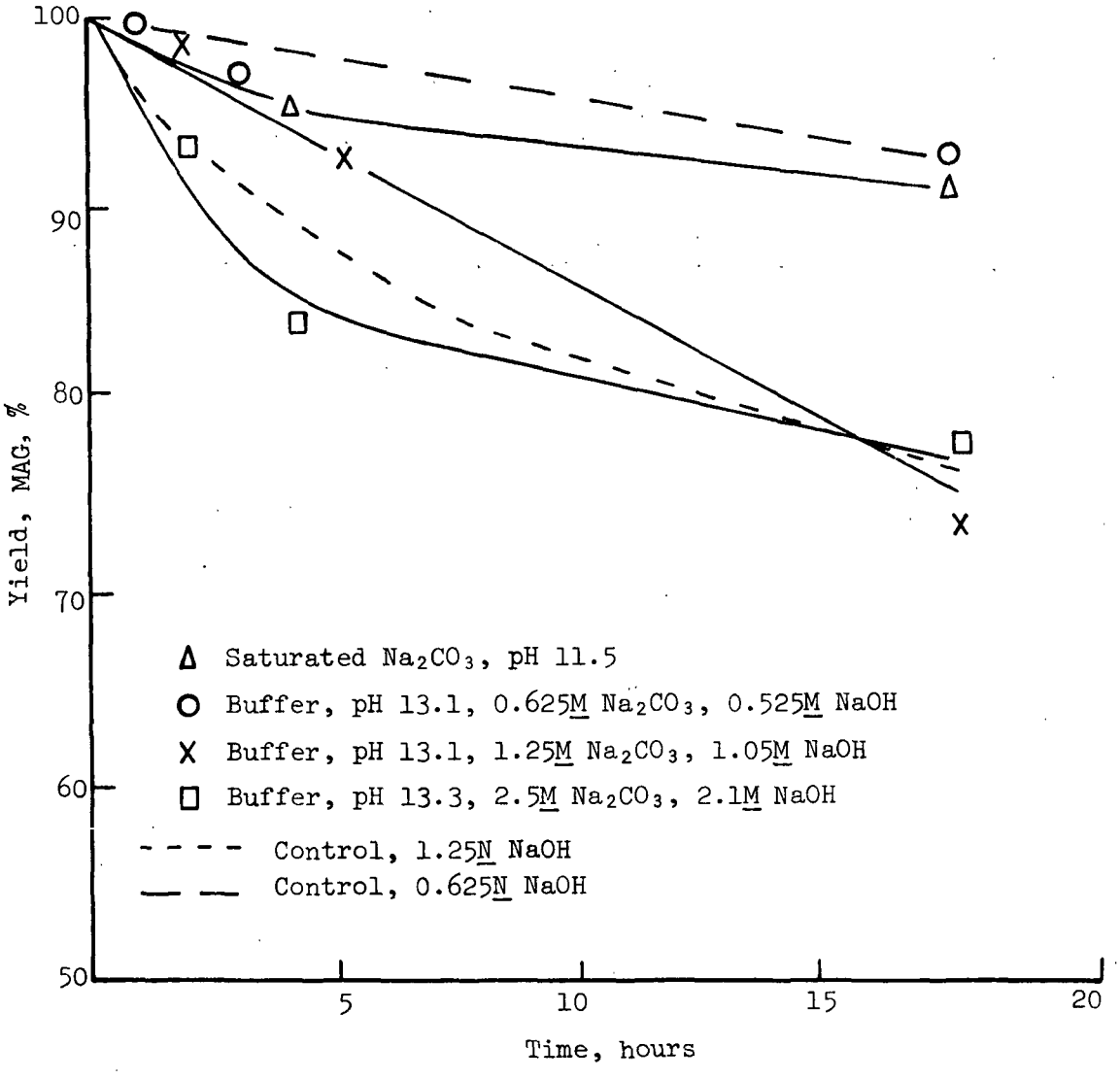
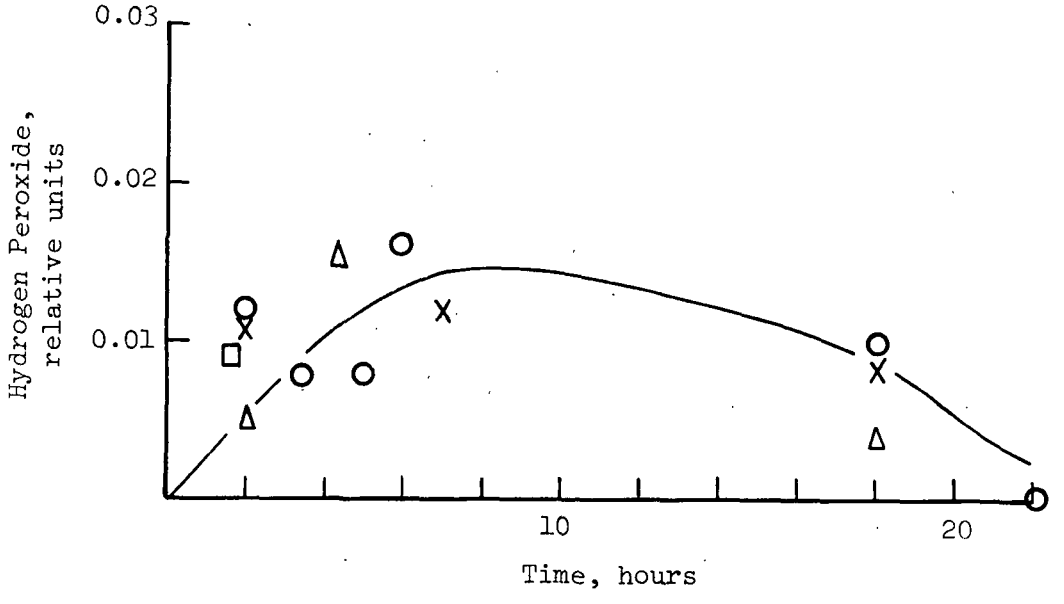


Figure 21. The Degradation of MAG with Time of Reaction in Different Buffered Solutions at 120°C and 100 psig O_2

The level of hydrogen peroxide attained in the different solutions is shown in Fig. 22. Very little difference is caused by different caustic concentrations or by pH levels greater than 13.1. This observation contradicts evidence in the literature suggesting a dependence of peroxide formation on the caustic concentration (47). It is not known whether the rate of formation of peroxide balances the rate of degradation over a wide pH range and carbonate concentrations in these studies, or if the literature data include total peroxide

instead of just hydrogen peroxide or if some other phenomenon is operating. No hydrogen peroxide could be detected during the reaction of MAG with sodium carbonate even though almost saturated solutions were employed. This apparent negative result probably results from the combined effects of a low rate of formation of peroxide due to the low pH coupled with a very high rate of decomposition due to the high carbonate content of the liquor.



○ 1.25N NaOH

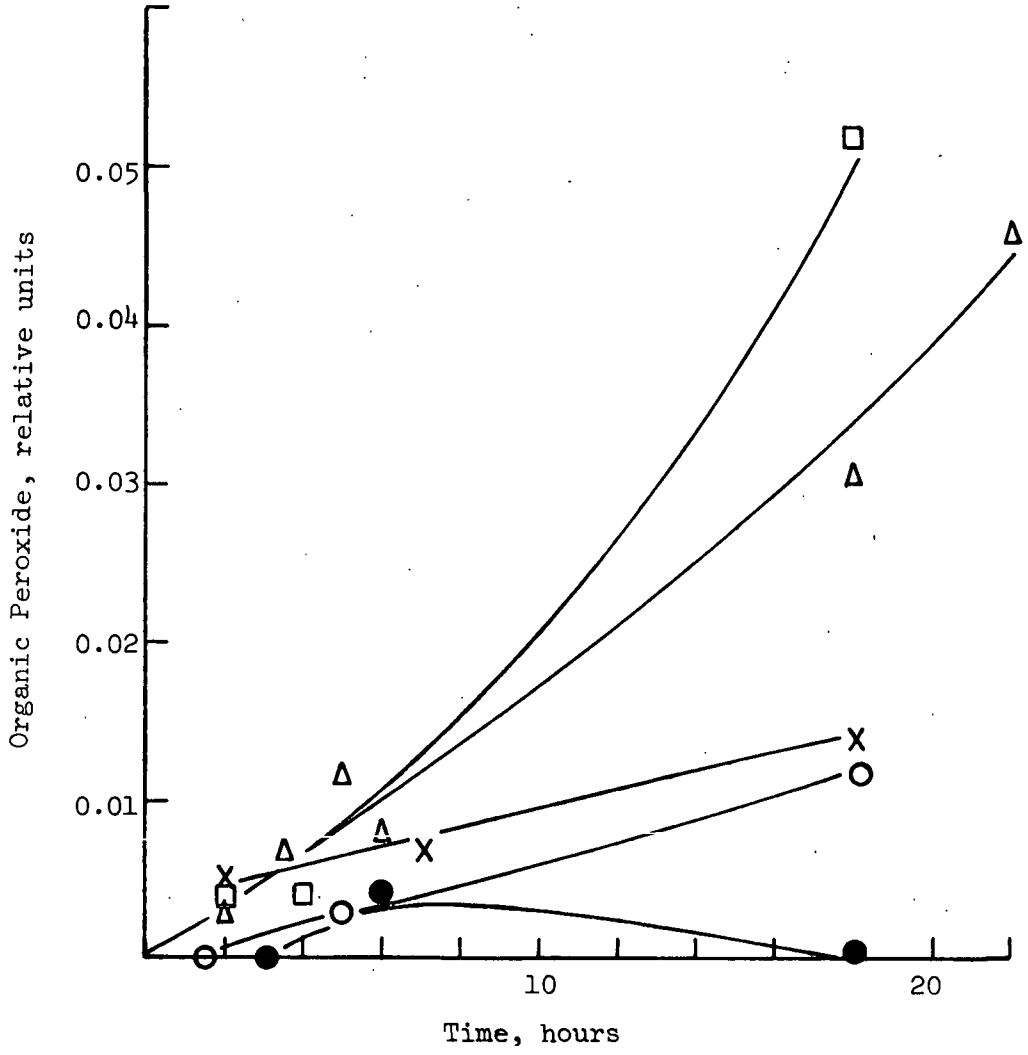
Δ Buffer, pH 13.1 — 0.625M Na_2CO_3, 0.525M NaOH

X Buffer, pH 13.1 — 1.25M Na_2CO_3, 1.05M NaOH

□ Buffer, pH 13.1 — 2.5M Na_2CO_3, 2.1M NaOH

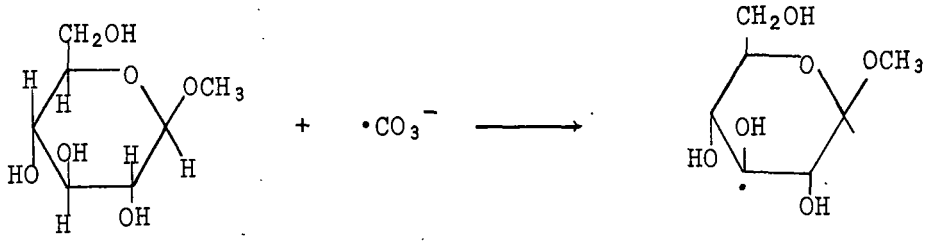
Figure 22. The Production of Hydrogen Peroxide when MAG is Reacted at 120°C in 100 psig O_2 and Different Alkaline Solutions

From the plots in Fig. 23, it can be seen that the formation of organic peroxides is influenced by the carbonate concentration as well as by pH. This behavior can be interpreted on the basis of the reaction mechanisms available in the literature. The first step is the formation of a carbonate radical:

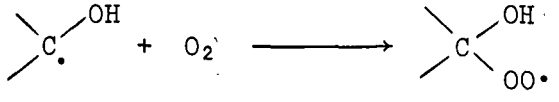


Δ 1.25N NaOH
○ 0.625N NaOH
● Buffer, pH 13.1 — 0.625M Na_2CO_3, 0.525M NaOH
X Buffer, pH 13.1 — 1.25M Na_2CO_3, 1.05M NaOH
□ Buffer, pH 13.3 — 2.5M Na_2CO_3, 2.1M NaOH

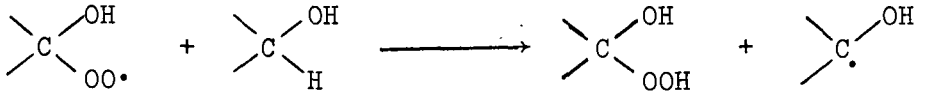
Figure 23. The Production of Organic Peroxides when MAG is Reacted at 120°C in 100 psig O_2 and Different Alkaline Solutions



The next step involves the facile addition of oxygen to the carbohydrate radical (35).



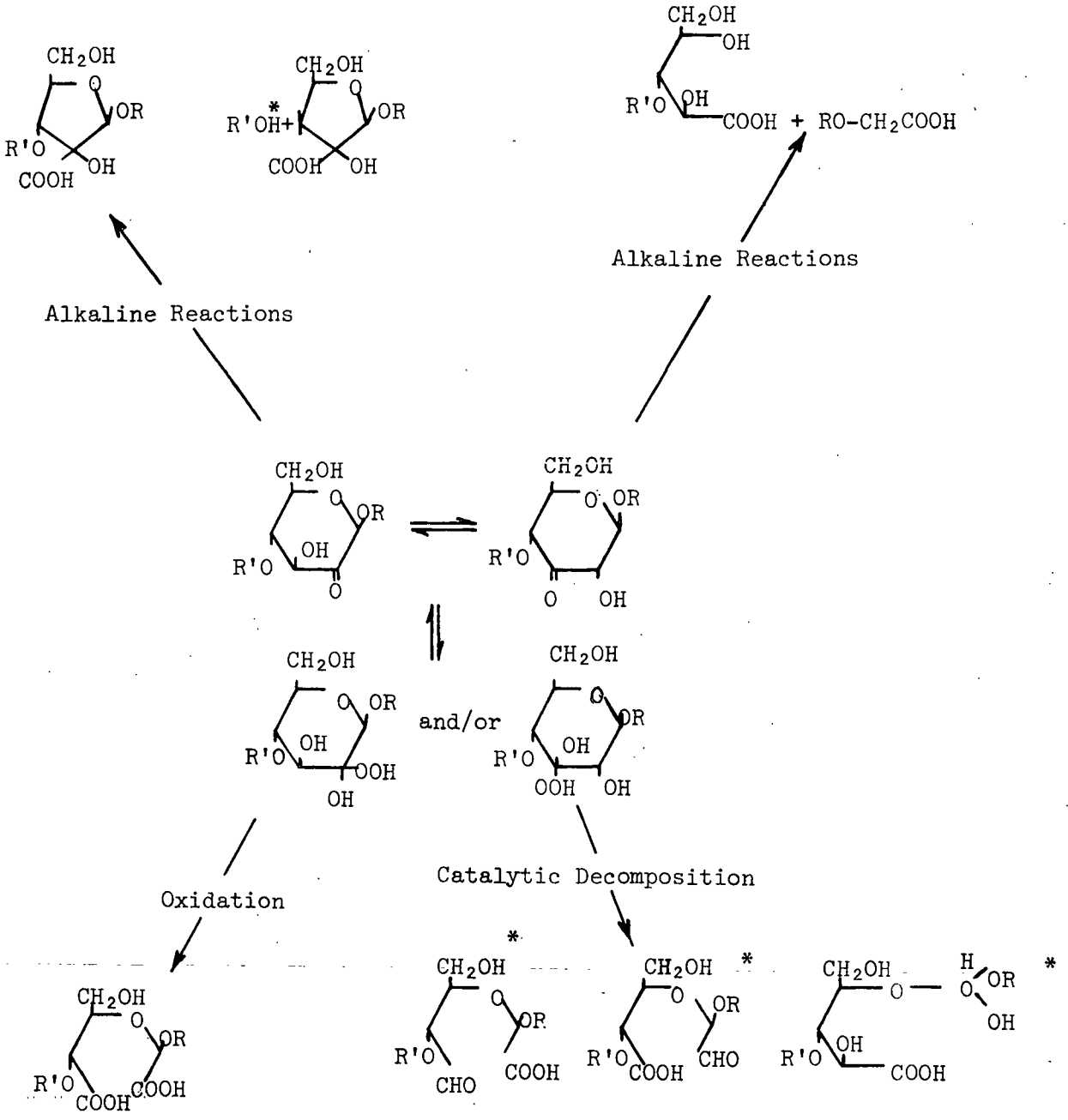
The subsequent reactions may or may not require an abstraction of hydrogen from an organic molecule. If it does, a propagating stage is introduced and the requirements for the Kolthoff-Medalia-Dewhurst recycling mechanism is complete (48).



The alkyl peroxides so formed can next react by means of a Karasch and Fono (49) mechanism to produce dialkyl peroxides characteristic of the prolonged oxidation of carbohydrates with oxygen. In sodium carbonate solutions at pH 11.5, this reaction is inhibited and no peroxides are detected. The reason for this behavior is not clear but must be related to the pH, the concentrations of HCO_3^- and $CO_3^=$ as well as to the slower formation of intermediate peroxides.

To date, these experiments have concentrated on the degradation of glycosidic rings by the reduced states of oxygen thought to be present during oxygen delignification reactions. The principal reaction products from these degradations are not the various organic peroxides described above (which are unique indications of degradative pathways), but oxidized glycopyranosyl rings capable of undergoing further reactions with both oxygen and alkali. Although the rate of degradation of these bonds (on a ring basis) is very small compared

to the rate of degradation by the peeling reaction (on a reducing group basis), there are thousands more glycopyranosyl rings available for reaction than there are reducing groups. The oxidative cleavage of these rings does not necessarily produce alkali-stable end groups but, as shown in Fig. 24, produces almost as often alkali- and acid-labile intermediates which lead to further yield and viscosity losses.



*Unstable in alkaline solution.

Figure 24. Schematic Representation of Possible Intermediates Derived from Organic Peroxides Formed from the Reaction of Glycosidic Bonds with Reduced States of O_2

UNCOMPLETED RESEARCH

The effect of carbonate and alkali upon aqueous solutions of oxygen has not yet been studied. It is anticipated that more complex solubility relationships of oxygen will occur in carbonate solutions than occurs in sodium hydroxide solutions. The potential radical interaction of carbonate ions with oxygen in those solutions may also contribute to a different chemical activity of oxygen compared to its behavior in noncarbonated solutions.

The effect of carbonated solution upon the reaction of oxygen and peroxide with reducing groups has not been explored. Whole new avenues of approach limiting peeling reactions are now possible based on the theoretical concepts of Isbell (50-56) and on the participation of carbonate ions in the radical reactions of certain organic peroxides. Also unexplored is the effect of transition metal ions on these reactions in general and especially on their anomalous and poorly defined reactions in oxygen-carbonate delignification reactions. Because of the rapid reaction rates which will be involved, these studies are best incorporated into the research originally proposed for Project 3265.

EXPERIMENTAL PROCEDURES

The procedures used in this report for the peroxide decompositions are similar to those that have already appeared in a previous report on this project (57). It should be noted that the sorption of metals from the previous series of reactions (57) onto the reactor used in these experiments interfered with the decomposition of peroxide. Decomposition reactions were continued until consistent results were obtained and the reactor was then used only for these studies. No evidence was obtained suggesting sodium borate or sodium carbonate

salts were sorbed into the reactor in sufficient quantity to interfere with succeeding experiments. The peroxide decompositions were carried out at room temperature. A number of decompositions were also conducted at 60° to show the trends were the same as at the lower temperature but the faster rates of degradation made the half-life estimations difficult. The borate buffers were prepared by adding sodium hydroxide or boric acid to saturated (25°C) $Na_2B_4O_7$ until the desired pH was achieved. Peroxide was then added to make the solution 0.17 mM in peroxide and the change in composition was followed by conventional analytical techniques (16,17,44,45).

The carbonate buffers were prepared by dissolving different ratios of sodium carbonate and sodium bicarbonate to give the desired pH levels. Care was taken to maintain a constant Na_2O_2 content of 38.8 g/liter despite the quantity of CO_2 present. The pH levels attained were 13.1, 11.3, and 8.4. A special mixture of carbonate-bicarbonate having a pH of 9.8 similar to that found in one example of the alkaline liquors from the Zimpro recovery (and potential pulping) process was also prepared from 9.9 g/liter Na_2CO_3 and 7.6 g/liter $NaHCO_3$ (on an Na_2O_2 basis).

The degradation of MBG by alkaline and carbonated peroxidic solutions was accomplished by reacting 20 mM MBG with 200 mM peroxide at 60°C dissolved in one of the following solvents: 2.5M NaOH, 1.25M NaOH, 1.25M Na_2CO_3 and saturated $NaHCO_3$ (about 1.5M). The formation of peroxides and the analysis of products by GLC techniques followed the procedures described by Weaver (44).

The reaction of MAG with oxygen in different alkaline solutions was accomplished by the procedure described previously using 100 psig O_2 at 120°C for varying lengths of time. The alkaline solutions employed were 1.25 and

0.625M NaOH and buffers such as 1.25 and 0.625M Na_2CO_3 (pH 11.5); 0.625M Na_2CO_3 and 0.525M NaOH (pH 13.1); 1.25M Na_2CO_3 and 1.05M NaOH (pH 13.1); 2.5M Na_2CO_3 and 2.1M NaOH (pH 13.3). The loss of MAG was measured by the Analytical Group and the formation of peroxidic products was accomplished by techniques described elsewhere (17).

CONCLUSIONS

1. Carbonate ions and/or bicarbonate ions can participate in radical reactions leading to the decomposition of peroxides and the degradation of glycosidic bonds. These studies suggest that hydrogen peroxide is decomposed both by catalytic degradations and by degradation related to its first dissociation constant.

2. The concentration of carbonate as well as pH is an important variable to consider in this reaction.

3. It is likely that the effect of the carbonate salt will manifest itself during oxygen delignification only when peroxides are intermediate reaction products.

4. Although hydroxyhydroperoxides and hydrogen peroxide react most readily with carbonate ion, their interaction can catalyze the decomposition of other organic molecules which would ordinarily be inert to the influence of carbonate ion.

5. The degradative reactions should lead to the production of alkali-labile carbonyl groups as well as to alkali-stable carboxylic acid derivatives in polysaccharides. Thus, both viscosity and yield losses can occur.

6. It is likely that both the pH and the concentration of the carbonate ions will have to be controlled to minimize these degradations during delignification reactions and that this might be achieved using some modification of the HOPES delignification procedure (58).

7. An alternative scheme would involve modifying the lignin and other peroxide percursors before reaction with oxygen so that peroxidic by-products are kept to a minimum. It is not known how this could be done economically.

COMPARISON OF GAS CHROMATOGRAPHY AND LIQUID CHROMATOGRAPHY FOR ANALYSIS OF OXIDATION PRODUCTS

In the work-up of our reaction mixtures from the flow reactor we encounter two major analytical problems. (1) The amount of material available for analysis is small, of the order of 5 milligrams at most, because of the relatively low concentrations of dissolved oxygen in our aqueous systems. (2) Separation of the acidic oxidation products from the original sugars. These two factors are discussed below for both systems of analysis, especially for the liquid chromatographic system, where we are now using a new universal detector; this has a moving wire to pick up the nonvolatile solute present in the solutions eluted from the column.

SENSITIVITY OF THE DETECTORS FOR THE TWO SYSTEMS

In a gas chromatograph the flame detector (FID) is extremely sensitive and a good peak can be obtained from a sample of 1 to 10 micrograms. However, carbohydrates have to be derivatized to give volatile samples, and the normal procedure is to treat 100 to 1000 micrograms of sample with 400 microliters of reagent to prepare the trimethylsilyl ethers. Of this 400 microliters, about 1% is injected on the column. So we have an efficiency of only 1% analysis, relating to our original sample. Some workers have carried out microderivatizations, but it is difficult to shake mixtures where the volume is so small.

In our liquid chromatograph the nonvolatile material in the solution eluted from the column is converted to methane and this passed into a FID detector similar to that in the gas chromatograph above. However, only 1% of the original solution is coated on the moving wire which transfers it into the evaporation and reaction tubes. So we have only 1% of the sensitivity per

injection compared with that for a gas chromatograph. This sensitivity, however, is far greater than we were able to get in the past with a UV detector.

To compensate for this 1% sensitivity, no derivatization is necessary, and we can concentrate our reaction product to a solid residue (as is done for GC work) and then dissolve this in a small amount (100 microliters) of water and inject a relatively large part of this (20 to 35 microliters) on the LC column. So this 20% injection contrasts favorably with the 1% injection for the GC system, and offsets to a great degree the 1% coating factor for the LC system.

Disregarding the background noise, which is greater for the moving wire detector than the FID detector in the LC system, we can sum up the efficiency of the two systems, as shown in Table VIII.

TABLE VIII

RELATIVE SENSITIVITIES OF DETECTORS IN GC AND LC SYSTEMS FOR CARBOHYDRATES[a]

	GC System	LC System
Original sample available for analysis, µg	1000	1000
Derivatization necessary	Yes	No
Sample injected on column, µg	10	200
Sample reaching detector, µg	10	2
Relative percent of original sample	1	0.2
Chemical stability of sample	Poor	Good
Biological stability of sample	Good	Poor
Reuse of sample not reaching detector	No	Yes
Background noise	Low	High

[a]Both systems use a FID detector, the GC directly, the LC through conversion of nonvolatile carbon to methane on a moving wire detector.

SEPARATION OF VARIOUS CARBOHYDRATES FOR THE TWO SYSTEMS

In both gas chromatography and liquid chromatography neutral sugars can be readily separated. In the GC system the sugars of lower molecular weight move more rapidly through the column. In the LC system the same rule holds (Fig. 25 and 26). To speed up the GC system, higher temperatures are needed; in LC systems a greater amount of a polar solvent (usually water) is used. Some LC separations have been carried out at temperatures up to 70°C to achieve better separations in a given time (59).

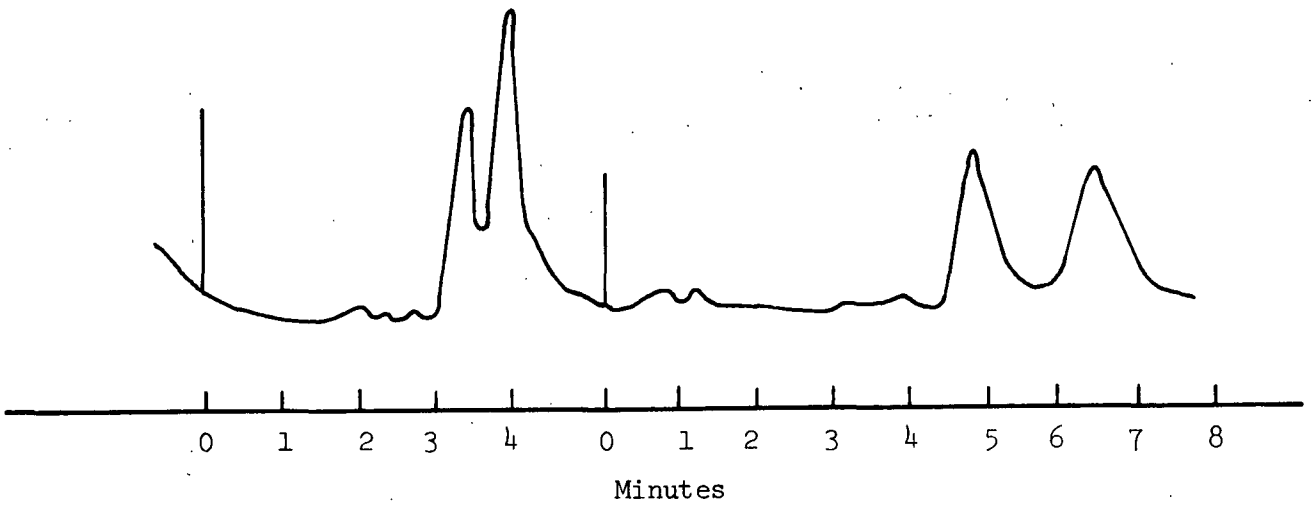


Figure 25. Separation of Glucose and Cellobiose with 70% and 80% MeCN Solvents, Respectively

In our GC system (OV-17 column) the oxidation products of sugars are not separated. Thus, both gluconic and cellobionic acid move at the same rate as the original sugars (Fig. 27 and 28). Because of this, earlier in this project we have destroyed the sugar in such a mixture by hot alkali (57). In an LC system with the Waters μ-Bondapak-Carbohydrate column carboxylic acids are absorbed when a neutral eluting agent (acetonitrile-water) is used. With an acidic eluting solvent, containing about 0.3% phosphoric acid, the carboxylic

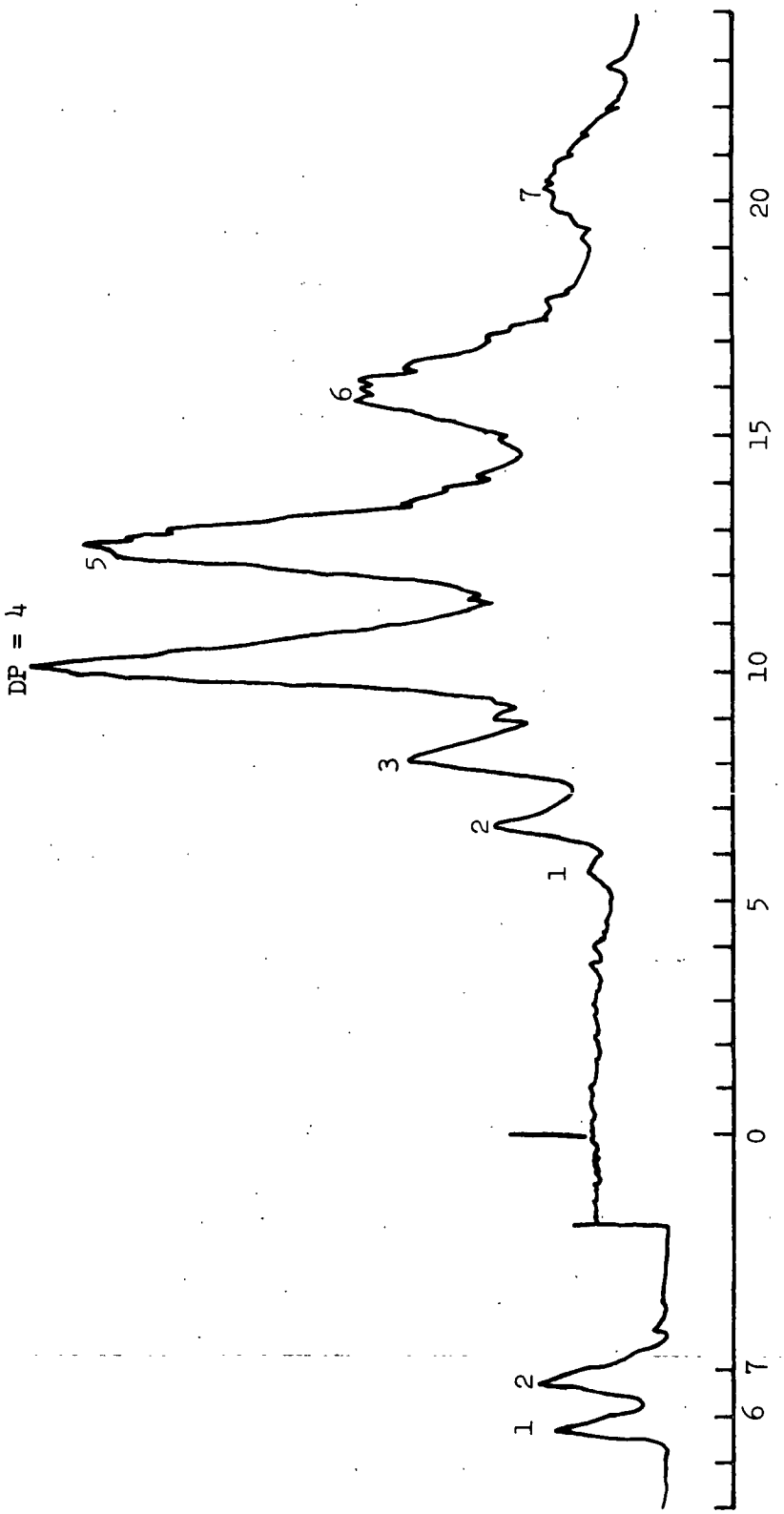


Figure 26. Liquid Chromatograph of Cellodextrin Mixture
75-25 MeCN-H_2O Solvent at 1 ml/min

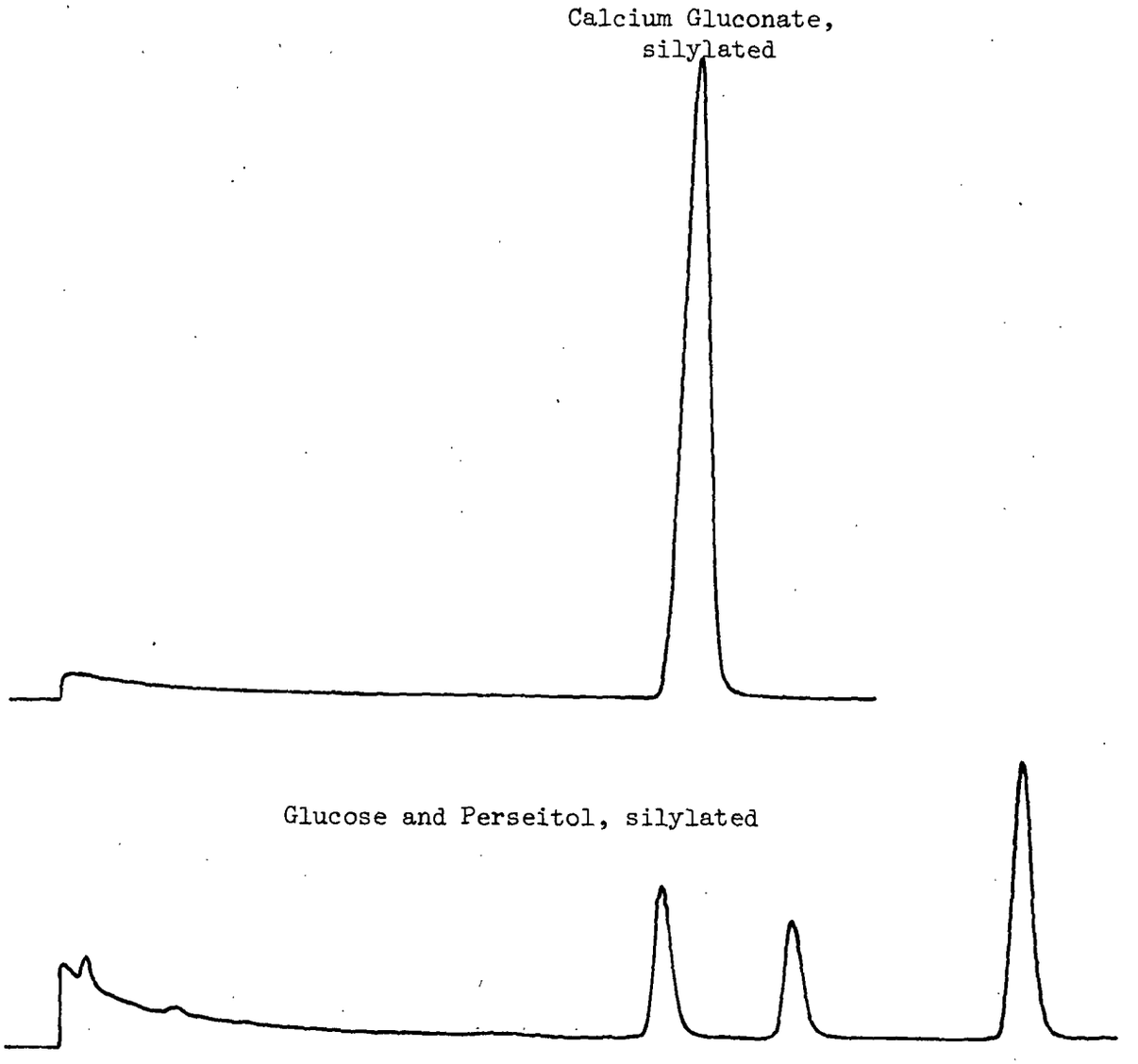


Figure 27. Similar Retention Times for Glucose and Gluconic Acid on the Gas Chromatograph (OV-17 Column, 130°C to 250°C, 4°/min)

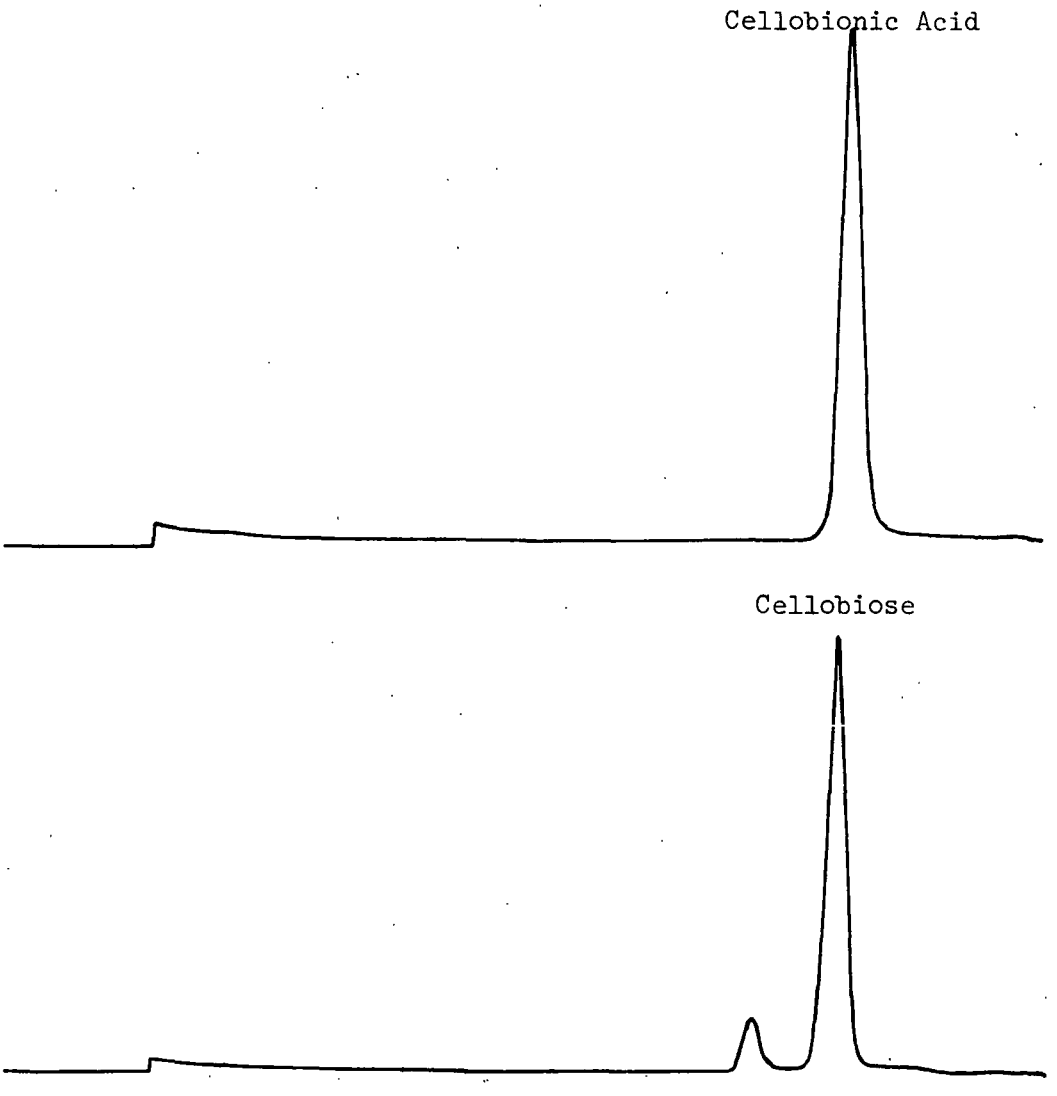


Figure 28. Similar Retention Times for Cellobiose and Cellobionic Acid in the Gas Chromatograph (OV-17 Column, 180°C to 250°C, 6°/min)

acids are not absorbed and move slowly through the column (Fig. 29). It is interesting that the phosphoric acid can be washed out of the column with water (Fig. 30). Weaker acids as acetic or trifluoracetic acid do not act similarly to phosphoric acid.

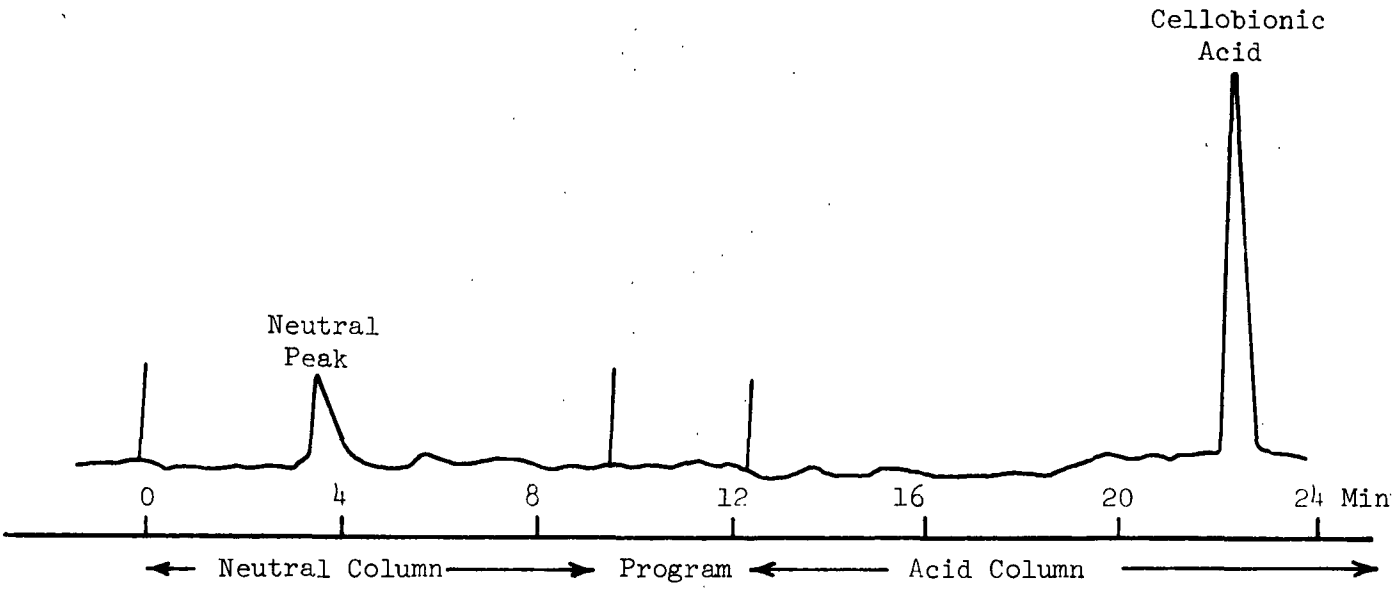
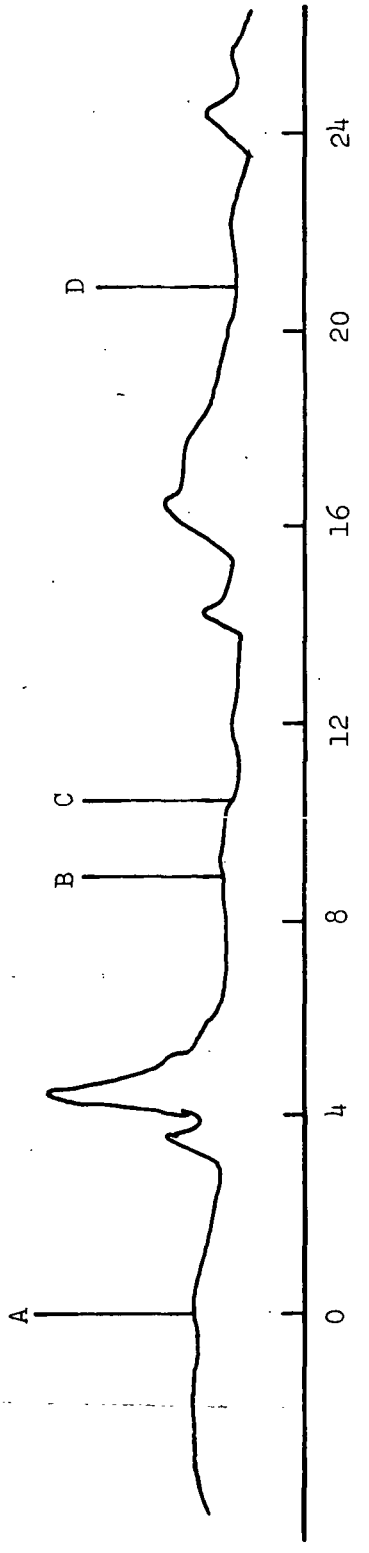


Figure 29. Sorption of Cellobionic Acid on Neutral Column and Desorption After Use of 70% MeCN and 30% (0.3% Phosphoric Acid)

Fortunately the basic groups on the Bondapak column do not affect the sugars, which are sensitive to alkaline systems (isomerization, rearrangement to saccharinic acid, or fragmentation such as peeling). Figures 25 and 26 show this. The Whatman Partisil-10 Pac column is somewhat similar in its action to the Waters column, in its sorption of carboxylic acids.

Only preliminary experiments have been carried out with the Bondapak column and it is not known if a slightly acidic column (very dilute phosphoric acid) will move the organic acids through at a slightly lower rate than the neutral sugars. With the acid concentration tried so far, the "acid column" moves cellobionic acid at the same rate as cellobiose.



A — Injection on Acid Column, B-C — Program Change to MeCN-H_2O, C — Injection Again of C-12 Acid, and D — 3rd Injection

Figure 30. Slow Washing out of Phosphoric Acid

One other difference noted with the Bondapak column, compared with the GC system, is in the case of the internal standards inositol and perseitol. These compounds move more rapidly than cellobiose in a GC system, and can be easily separated from each other, being C-6 and C-7 alcohols, respectively. In the LC system, however, they both move at the same speed as cellobiose, so that they cannot be used as internal standards or reference compounds (see Table IX). A new series of compounds will have to be used in the LC systems.

TABLE IX

SEPARATIONS ACHIEVED ON GC AND LC COLUMNS[a]

	GC System	LC System
Neutral sugars	Very good	Good
Internal standards	Good	Poor
Neutral and acidic sugars	Poor	Good
Separation according to molecular wt.	Good	Poor
Sharpness of peaks	Good	Fair
Time of separations	Good	Fair
Faster movement on column with	Higher temperature	More polar solvents

[a]The two columns compared above are on OV-17 column for a GC system, and a Waters-Bondapak column for an LC system. The sugars have to be derivatized for the GC system.

USE OF OTHER COLUMNS IN LIQUID CHROMATOGRAPHY

So far our efforts have been confined to the Waters column, which was tailor-made for carbohydrate separations, and which has slightly basic groups to give a polar surface. Some workers have used silica columns (60) with solvent mixtures containing ethyl acetate or methyl ethyl ketone. Others have

used cation exchange resins containing lithium as a "counterion" (59); these were used at elevated temperatures. It may be possible that good separations of acids and neutral sugars can be achieved with these columns. The elution times for these columns are much slower than with the Bondapak column.

COMBINED USE OF GC AND LC SYSTEMS

The Bondapak column could be used to achieve a separation of neutral and acidic carbohydrates. The neutral fractions (99% draining below the coater in the moving wire detector) can be collected, concentrated and analyzed by GC. Then the column can be treated with phosphoric acid, the acids eluted (see Fig. 29), treated with a weak anion resin to remove the phosphoric acid and the filtrate concentrated and analyzed by GC. We would need two internal standards, the usual inositol or perseitol for the neutral fractions, and another one for the acidic fractions. This latter standard would have to be acidic, and one possibility is α-glucoheptonic lactone, which is commercially available and should move much slower than cellobionic acid on a GC system.

EXPERIMENTAL

Operation of the Moving Wire Detector

Briefly, the function of this apparatus (Fig. 31) is to (a) remove the volatile solvent from effluent coming from a chromatographic column, and (b) convert the carbon in the nonvolatile residue to methane which is measured in a FID detector, similar to that in a gas chromatograph. The wire coming from the right goes through a cleaner to remove any residual organic material, then picks up effluent on a coating block, passes through an evaporator zone to remove solvent, and then through an oxidizer to convert all carbon in the residue to carbon dioxide. This gas is then swept by air into an entrainer where it is

mixed with nitrogen and hydrogen, and reduced to methane. The latter is led into the FID detector.

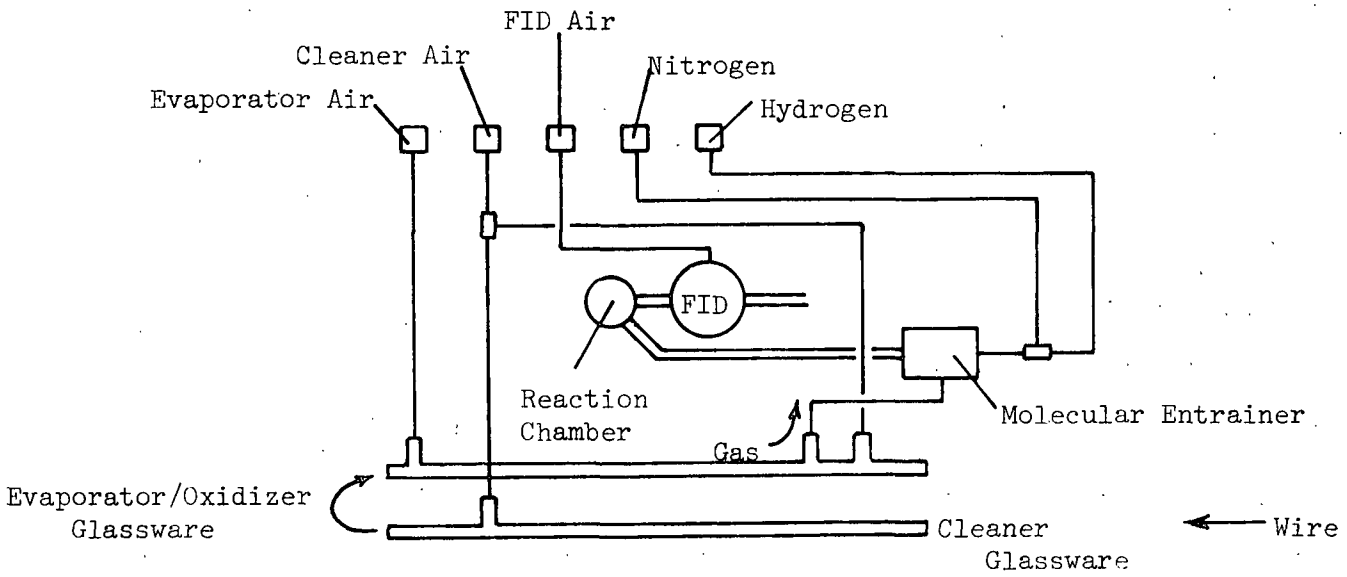


Figure 31. Schematic Diagram of Detector Assembly (61)

Fractionation of Glucose and Cellobiose on a Waters Bondapak-Carbohydrate Column

This separation is shown in Fig. 25. With 70% acetonitrile the two peaks are just pulling apart, and with 80% acetonitrile there is a very good separation. When a mixture of 60% acetonitrile is used, only one peak is observed.

Fractionation of a Mixture of Cellodextrins

This is shown in Fig. 26. Seven peaks are observed, starting with a very small one for glucose, and two large ones for cellotetraose and cellopentaose. A similar chromatogram has been obtained with GC of the trimethylsilyl derivatives. However, in the GC runs the DP = 6 and DP = 7 fractions were at the high end of the temperature programming (350°C) and came through with a rapidly rising base line.

The small DP = 7 peak may represent the limits of solubility of the higher fractions in water. The original mixture had an average DP = 4 (based on iodine titration) and only part of it (about 80%) dissolved in water. There may be a small amount of DP = 8 fraction present; the trace trails at this point. Some programming was tried, with a higher percentage of water added at the DP = 6 stage, but it is still difficult to note an appreciable peak beyond DP = 7.

Creation of an "Acid" Bondapak Column

This column is normally operated in a "neutral" condition with acetonitrile and water. The manufacturers describe it as a "special purpose column packing designed specifically for sugar separations." Apparently it has basic groups which create a polar surface; however, the basicity is not enough to harm any sugars, but it is enough to absorb carboxylic acids. These acids can be desorbed only by the use of 0.3 to 0.5% phosphoric acid mixed with acetonitrile. This phosphoric acid takes effect in desorbing the carboxylic acid in about 9-15 min (flow rate of 1 ml/min), and the same amount of time is required to wash the phosphoric acid from the column, i.e., conversion from an acid column back to a neutral column.

In Fig. 29 the effect of phosphoric acid is shown. Cellobionic acid normally gives a small neutral peak not sorbed by the neutral column. When the eluting solvent is changed from 70% acetonitrile and 30% water (A) to 70% acetonitrile and 30% of 0.3% phosphoric acid (b) the cellobionic acid is eluted as a sharp peak.

When a solution of cellobionic acid is injected on the acid column, with the eluting solvent B being used, two peaks are obtained; one is the neutral peak (possibly the lactone) and the larger one is the acid (Fig. 30).

When eluting solvent A was used on the acid column, partial desorption of the cellobionic acid occurred, also shown in Fig. 30. Another injection, made 10 min after the initial use of solvent A, showed complete sorption of the acid peak.

Similar behavior was shown with gluconic acid, and with glutaric acid. Attempts to desorb acids with acetic acid or with phosphoric acid failed.

Chemical Breakage of Wire

We have been using 0.5% phosphoric acid in our eluting solvent and this may corrode and embrittle the wire. Breakage seems to occur in the cleaner tube, when the latter is operated at the higher temperature settings (900°C). We have found that breakage does not occur when the lower setting (400°C) is used. The Phillips people (61) assure us that the acid will not embrittle the wire but we are not sure about this. Suitable recorder peaks were obtained at the lower cleaner temperature.

Potassium Cellobionate

This was an adaptation of the method of Moore and Link (1). Modifications were necessary as cellobiose is not very soluble in water and less so in methanol. Also the potassium salt precipitates as a sirup initially and becomes a granular precipitate only when a large excess of alcohol, relative to water present, is used.

Cellobiose (3.8 g) is dissolved in 20 ml water at 55°C; this takes about 10 min of stirring. The solution is then added to 50 ml methanol; a clear solution results. Iodine (5.7 g) is added to this solution; only part of the iodine will dissolve, because of the large amount of water present.

Alcoholic KOH (4% in methanol) (65 ml) is diluted to 100 ml with methanol. This is added to the cellobiose-iodine mixture during 10-15 min; the latter is maintained at 40°C in a water bath (crystallizing dish) placed on a magnetic stirrer.

After the KOH is all added, the solution is stirred for 10 min. The precipitated potassium cellobionate is often sticky at this stage and will prevent the stirring bar from moving. More KOH (50 ml, diluted to 100 ml) is added during 10 min, again at 40°C. The solution is stirred a final 10 min and is now light yellow in color.

The cloudy solution is decanted from the precipitated sirup. The latter is dissolved in 5 ml water and then added slowly to 100 ml methanol. A white precipitate is formed; this settles quickly. The mixture is centrifuged, the precipitate shaken with 50 ml methanol, centrifuged and this repeated twice with 50 ml acetone. The product, dried over phosphorus pentoxide, is a white powder (fraction A), which is hygroscopic, and should be shielded from the moist atmosphere.

Two minor fractions are obtained. The first, fraction B, is obtained as a precipitate from the combined methanol and acetone washings of A above; this is some more potassium cellobionate. Fraction C is obtained when the original 5 ml of aqueous solution is poured into methanol; it is a small amount of hardened yellow precipitate adhering to the bottom of the beaker, distinct from fraction A which is in suspension in the liquid. However, fraction C could not be precipitated from water into methanol; it may be some unreacted cellobiose.

The main fraction (A) weighed 3.0 g; this is a good yield starting from 3.8 g of cellobiose. The product gave a negative Fehlings test so there is no cellobiose present. Conversion to the trimethylsilyl derivative with TriSil

concentrate and dimethyl sulfoxide and gas chromatography gave only one peak, at 11.5 min retention time (see Fig. 28). This is the same time as for cellobiose, so the aldonic acid cannot be separated from the original aldose by GC.

Another batch was made similarly from 7.6 g of cellobiose; the yield of potassium salt was 5.6 g, not quite so good a yield as in the first run.

FUTURE WORK

With the preparation, analysis and control of high concentrations of dissolved oxygen well in hand, reactions of carbohydrates will be studied in the flow reactor for various temperatures and for solutions of pH ranging from 8 to about 13. The systems will be analyzed for unreacted carbohydrate and for oxidation products. The reactions at the higher temperatures and pH will be quite rapid and very short reaction times will be used. For others the time of reaction will be as great as 10 min or more. If time allows, some reactions with catalysts and compounds used as inhibitors in glucosidic bond cleavage (a much slower reaction) will be carried out.

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